

A NEW THEORY OF FLUIDS: THE "TUNNEL" MODEL

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Summary

A new method for calculating the thermodynamic properties of liquids and compressed gases is proposed, based on a model in which lines of molecules move almost one-dimensionally in "tunnels", the walls of the tunnels being formed by neighbouring lines of molecules. This picture is related to the "cell" model, but it is a disordered picture, as is appropriate in a model for fluids, and the problem of the "communal entropy" which besets the cell model, does not arise. The method is applied to the hard-sphere fluid and the calculated pressure/volume isotherm is in very much better agreement with the expected isotherm than either the cell theory or the superposition theory, and also in rather better agreement than the virial expansion truncated after five terms.

I. INTRODUCTION

In spite of many attempts no completely satisfactory theory of the liquid state has yet been developed. It is indeed possible to find much useful information by a direct Monte Carlo evaluation of the phase integral for large groups of molecules (Wood and Jacobson 1957) or by direct solution of the equations of motion (Alder and Wainwright 1957), but both of these approaches require such enormous amounts of computation that simpler methods would be very valuable. Theories based on the "superposition" approximation (Hirschfelder, Curtiss, and Bird 1954) have proved to be quantitatively unsatisfactory. The "cell" model (Hirschfelder, Curtiss, and Bird 1954) in which molecules are imagined as moving almost independently in cells formed by their neighbours, has for some time appeared the most promising approach. However it appears now that the cell theory is really more satisfactory as a theory of *solids*, because it starts from an *ordered* arrangement of molecules. Attempts to arrive at a theory of fluids by introducing disorder, by allowing for multiple occupation of cells and correlation effects (de Boer 1954; Barker 1956), have met with many difficulties. Nevertheless the basic idea of the cell theory, that one should divide the whole fluid into subsystems sufficiently simple to permit calculation of their properties, is very valuable. The theory proposed here follows this idea, with the subsystems chosen as lines of molecules moving almost one-dimensionally in tunnels, the walls of the tunnels being formed by the neighbouring lines of molecules. Because each subsystem contains very many molecules it is not necessary to take account of the fluctuation of the numbers of molecules in each subsystem; thus the problem of "communal entropy" does not arise. And because the subsystems are approximately one-dimensional we can calculate their properties, since the partition function or phase integral for a one-dimensional system can be evaluated exactly.

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This picture is essentially disordered as it should be, and it allows for the possibility of relatively easy diffusional movement (cf. Wood and Jacobson 1957) since a molecule can easily jump out of its tunnel to a gap in the walls. Both of these are attractive features in a model for fluids.

In using the model to calculate thermodynamic properties it is necessary to assume in the first instance that the motions of the molecules along and across the tunnel are *separable*, so that the phase integral for the whole system is a product of the phase integral for a one-dimensional fluid and the phase integral for independent vibrations of the molecules at right angles to the tunnel axis. It is also implied that the motions of the molecules in different tunnels are independent, except that the molecules in one tunnel form part of the walls of other tunnels. It should be possible to improve these assumptions in much the same way as the cell theory has been refined (Barker 1956). The purpose of this paper is to show that even in very crude form the "tunnel model" gives a good approximation to the properties of the hard-sphere fluid. Since the major weakness of the cell theory is that it does not account correctly for the volume exclusion of the molecules, and so gives incorrect values for the entropy of liquids, this suggests that the tunnel model should be a useful starting point for a theory of real fluids.

II. THE HARD-SPHERE FLUID

We consider a system of N hard-sphere molecules of diameter D in a volume V . We wish to evaluate the phase integral

$$Q(N, V) = (1/N!) \int \dots \int e^{-U/kT} dx_1 dy_1, \dots, dz_N, \dots \quad (1)$$

where the potential energy U is $+\infty$ if any two molecules lie within distance D of each other, and zero otherwise. We imagine the volume V divided into a number K of hexagonal cylinders arranged in close-packing, as shown in section in Figure 1. We suppose that each cylinder or tunnel contains M molecules, so that KM is equal to N , that the length of each cylinder is lM , and that the distance between the centres of neighbouring cylinders is r . It follows that the cross-sectional area of each tunnel is $\sqrt{3}r^2/2$, so that the total volume V is given by

$$V = K.lM.\sqrt{3}r^2/2. \quad \dots \dots \dots (2)$$

But since KM is equal to N it follows that

$$\frac{V}{N} = \frac{\sqrt{3}}{2}lr^2. \quad \dots \dots \dots (3)$$

Following the ideas set out in Section I we take as our approximation to the phase integral Q the following form:

$$Q(N, V) = (1/N!)[N!/(M!)^K] \left[\int_0^{lM} \dots \int_0^{lM} e^{-U/kT} dz_1, \dots, dz_M \right]^K A_f^N. \quad \dots \dots \dots (4)$$

The factor $N!/(M!)^K$ is the number of ways of distributing the N molecules between the K tunnels, and A_f is the "free cross-sectional area" in the tunnels

(cf. Fig. 1). The potential energy of the one-dimensional system of M molecules in the length lM is denoted by U' . The integral appearing in (4) can be expressed in terms of the phase integral $Q'(M, lM)$ for a one-dimensional system of M molecules in length lM , since by definition we have

$$Q'(M, lM) = (1/M!) \int_0^{lM} \dots \int_0^{lM} e^{-U'/kT} dz_1, \dots, dz_M. \quad (5)$$

Thus we find

$$Q(N, V) = [Q'(M, lM)]^K A_f^N. \quad (6)$$

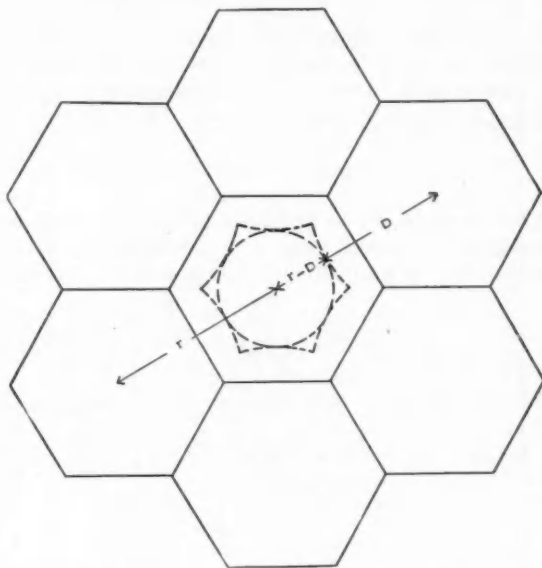


Fig. 1.—Cross section of tunnels, showing "free cross-sectional area".

But the phase integral for a one-dimensional system can be evaluated exactly (see, for example, Prigogine 1957, Ch. 6); for the hard-sphere case the result is

$$Q'(M, lM) = e^M (l-D)^M. \quad (7)$$

Substituting in (6) we find

$$Q(N, V) = e^N (l-D)^N A_f^N. \quad (8)$$

In the low density limit D is negligible compared with l and A_f becomes equal to $\sqrt{3}r^2/2$, so that $Q(N, V)$ becomes

$$\begin{aligned} Q(N, V) &= e^N l^N (\sqrt{3}r^2/2)^N \\ &= e^N (V/N)^N. \end{aligned} \quad (9)$$

This is the correct result for an ideal gas. The cell theory, by contrast, omits the factor e^N , which is the "communal entropy" term. Thus by using the tunnel model we have automatically made allowance for the communal entropy. Another way of saying this is that the model makes allowance for density fluctuations in a natural way.

At higher densities we will approximate the free cross-sectional area by the area of the largest circle that can be inscribed in the tunnel without intersecting regions excluded by molecules at the centres of neighbouring tunnels (cf. Fig. 1). Thus we assume

$$A_f = \pi(r-D)^2. \quad (10)$$

This is a reasonable approximation provided that $r-D$ is less than $\frac{1}{2}r$, so that the inscribed circle lies wholly within the hexagonal cylinder; this condition is satisfied at the densities with which we are concerned here.

From equations (10) and (18) we find

$$Q(N, V) = [\pi(r-D)^2(l-D)e]^N. \quad (11)$$

We have not so far specified r and l , except that they must satisfy equation (3). It is reasonable to choose l and r to maximize $Q(N, V)$, subject to the restriction imposed by equation (3). It is easy to show that this leads to the result

$$r = l = \left(\frac{2V}{N\sqrt{3}} \right)^{\frac{1}{2}}. \quad (12)$$

The Helmholtz free energy and pressure for the system are given by

$$F = -kT \ln Q(N, V); \quad (13)$$

$$P = -\partial F / \partial V. \quad (14)$$

Using (11) and (12) we find

$$P = (NkT/V_0) / [(V/V_0) - (3/2)^{\frac{1}{2}}(V/V_0)^{\frac{1}{2}}], \quad (15)$$

where V_0 is the close-packed volume of the system, equal to $ND^3/\sqrt{2}$.

Values of PV_0/NkT calculated from equation (15) are shown as curve T_1 in Figure 2; values obtained by other methods are given for comparison.

Calculations have also been made using a different and probably rather better approximation for the free cross-sectional area A_f , namely

$$A_f = \pi(r-D')^2, \quad (16)$$

where D' is the average closest difference of approach of a molecule of diameter D to the line of centres of a line of similar molecules with uniform spacing l ; D' is given by the equation

$$D' = (D^2/l) [\sin^{-1}(l/2D) + (l/2D)\sqrt{(1-l^2/4D^2)}]. \quad (17)$$

We substitute from equation (16) in equation (8), eliminate r using equation (3), and determine the value of l which maximizes $Q(N, V)$ by differentiation. In terms of the variable $u=l/D$ we find

$$Q = \{\pi e D^3 (u-1)^3 [(3/2)\sqrt{1-u^2/4} - \sin^{-1}(u/2)/u]\}^N, \quad \dots (18)$$

$$V/V_0 = \sqrt{(3/2)u[(2-u)\sin^{-1}(u/2)/u + (3u-2)\sqrt{(1-u^2/4)/2}]^2}. \quad \dots (19)$$

The pressure can be calculated from the equation

$$P = kT(\partial \ln Q / \partial u) / (\partial V / \partial u), \quad \dots (20)$$

where the derivative $(\partial V / \partial u)$ is to be calculated using equation (19).

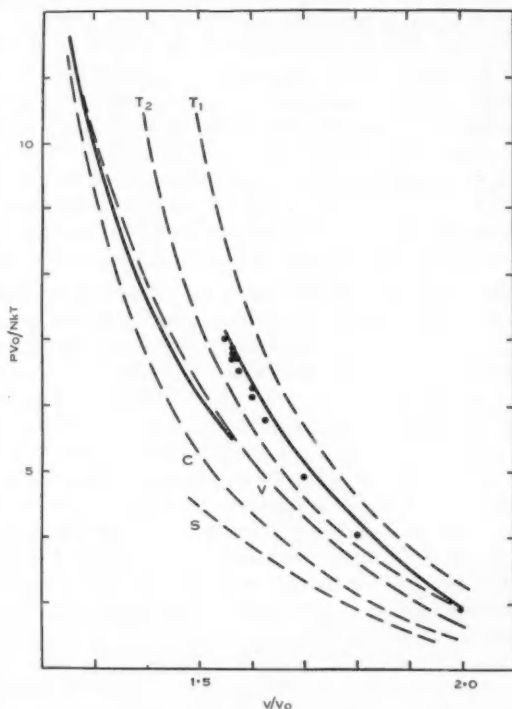


Fig. 2.—Pressure/volume isotherm for hard-sphere system. Solid curves, results from detailed molecular dynamics. ● Monte Carlo calculations; T_1 , tunnel model, equation (15); T_2 , tunnel model equations (18)–(20); C , cell or free volume theory; V , 5-term virial series; S , superposition theory. All data except T_1 and T_2 from Wood and Jacobson (1957).

Pressures calculated from equations (18)–(20) are plotted as the curve T_2 in Figure 2. It is interesting to note that if we use equation (16) but assume $l=r$, that is, if we do not maximize with respect to l , then the calculated pressures are even higher than those given by (15).

III. DISCUSSION

The best available information on the hard-sphere system is that derived by Monte Carlo evaluation of the phase integral and by calculations on detailed molecular dynamics; the isotherm derived from these results will be referred to as the "numerical" isotherm. According to these calculations the system shows a transition in the region $V/V_0=1.5$ to 1.6 . For V/V_0 larger than 1.6 the behaviour is fluid-like, with relatively free diffusion; for V/V_0 less than 1.5 the behaviour is solid-like. The pressures calculated from the tunnel model using equations (10) and (15) (curve T_1) show reasonably good agreement with the fluid branch of the numerical isotherm, and very poor agreement with the solid branch. This is to be expected since the tunnel model is a disordered, fluid-like model. The pressures calculated from the tunnel model using equations (16)–(20) show somewhat better agreement; indeed the largest difference between the tunnel model values and the Monte Carlo values is only about twice the largest difference between the Monte Carlo values and those deduced from the calculations on detailed molecular dynamics. The tunnel model isotherm appears to be approaching the (extrapolated) numerical fluid isotherm at high densities in much the same way as the cell or free volume isotherm approaches the solid isotherm. It seems clear from these results that the tunnel model is a genuine model for the fluid, as distinct from the solid, state.

The pressures calculated from the cell or free volume theory show reasonable agreement with the solid branch of the numerical isotherm at high densities, but very poor agreement with the fluid branch, in accordance with the view that the cell model is more appropriate for solids. The pressures calculated from the "superposition" theory show very poor agreement with either branch of the isotherm; they are closer to the solid branch than to the fluid branch. The virial series including coefficients up to the fifth gives pressures lying below the fluid branch; the fact that it gives good agreement with the solid branch is probably coincidence since higher virial coefficients must raise the curve towards the fluid branch. The tunnel theory actually gives better agreement with the numerical fluid isotherm than the virial series with five virial coefficients. This is interesting when one remembers that it is only for the hard-sphere potential that virial coefficients beyond the third have been calculated. It is also known that the virial series cannot describe the properties of the liquid state—for the hard-sphere system there is of course no liquid state. The tunnel model, on the other hand, should be capable of describing the liquid state at least as well as the cell theory, and probably, on the indications of the results given here, considerably better.

The procedures involved in applying the tunnel model to real fluids, for example to inert gases using the 12–6 potential, are closely analogous to those used by Lennard-Jones and Devonshire (1937) in using the cell model. Instead of "smearing" the neighbours over a spherical surface they must be "smeared" over the surface of a cylinder. In addition of course the one-dimensional phase integral must be evaluated using known methods. It is hoped that later publications will describe detailed calculations on critical isotherms and vapour pressures.

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THE REACTION OF CARBON WITH CARBON DIOXIDE AT HIGH PRESSURE

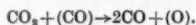
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Summary

A study has been made of the reactions of purified carbon with carbon dioxide at pressures up to 40 atm and in the temperature range 790–870 °C. The effect of carbon monoxide has been examined by adding varying proportions of this gas to the carbon dioxide supplied to the reactor bed.

At high carbon dioxide and carbon monoxide partial pressures, the rate of formation of carbon monoxide is greater than would be expected from the mechanism proposed by Gadsby *et al.* (1948). A mechanism has been proposed whereby the increased rate may be explained by additional steps involving the interaction of a carbon dioxide molecule with an adsorbed carbon monoxide to produce adsorbed oxygen, thus:



A general rate equation has been derived which includes this step and satisfies the experimental results. The reverse mechanism by which carbon monoxide can disappear is not the simple reverse of the forward process and at high pressures equilibrium cannot be expressed by the usual expression derived for the simple single-stage reversible process.

The possible nature of active sites has been examined by studying the reactivity of a series of chars prepared at different temperatures. The reactivity appears to be related to the oxygen content of the chars and the type of active centres involved may be different from those which control the carbon-steam mechanism.

I. INTRODUCTION

The reaction between carbon and carbon dioxide has been studied extensively at pressures up to 1 atm. It was first shown by Boudouard (1899*a*, 1899*b*, 1900) that the process was reversible and could be represented by the general equation



Rhead and Wheeler (1911) showed that at temperatures above 800 °C equilibrium could be attained but that at this temperature it required 70 hr to attain equilibrium and that the rate of conversion of carbon dioxide was about 116 times that of the conversion of carbon monoxide. Dent and Cobb (1929) showed that the composition of the gases at equilibrium could be affected by the nature of the carbon.

The mechanism of the reaction has been explained on the basis of an adsorption process where carbon dioxide breaks down at the carbon surface to form carbon monoxide and an oxygen atom, this latter being in the adsorbed state.

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The oxygen atom can then react with carbon to form molecular carbon monoxide. These steps are represented by the equations



To explain the retarding effect of carbon monoxide, two theories have been advanced. That of Gadsby *et al.* (1948) suggests that carbon monoxide can be adsorbed on the carbon surface and compete equally with oxygen for active sites. The process is represented by the reaction thus,



These three steps, equations (2), (3), and (4), can be used to derive a rate equation in which the rate of appearance of carbon monoxide can be expressed as a function of the partial pressures of carbon dioxide and carbon monoxide and the rate constants of the individual equations. It is given by

$$\text{Rate} = k_1 p_{\text{CO}_2} / (1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}). \quad \dots\dots\dots (5)$$

A further suggestion by Semechkova and Frank-Kamenetskii (1940) and by Reif (1952) and recently by Blackwood and McTaggart (1959) is that the retarding effect of carbon monoxide could also be explained by the prevention of breakdown of carbon dioxide by a reversal of equation (2). If equation (4) is eliminated and equation (2) is reversible then a rate equation identical in form with equation (5) can be derived. It is clear that either mechanism will express the results at atmospheric pressure and although there is some evidence to suggest that the second explanation is the more likely, there is no conclusive proof.

A third possibility has been suggested by Evropin, Kulkova, and Temkin (1956) that, on the evidence obtained by studies of isotopic exchange, the retarding action of carbon monoxide is not due to adsorption but to the reverse mechanism



Equation (6), together with equation (4), has led to the development of a rate equation

$$\text{Rate} = k_1 [p_{\text{CO}_2} / (1 + k' p_{\text{CO}})]^{0.5}. \quad \dots\dots\dots (7)$$

If the reverse process, expressed by the reverse of equation (6), is used in conjunction with equations (2), (3), and (4), then a rate equation can be derived which includes the disappearance of carbon monoxide due to the formation of carbon and carbon dioxide. Such a rate equation has been developed by Semechkova and Frank-Kamenetskii (1940) and is given by

$$\text{Rate} = 2 \frac{k_1 p_{\text{CO}_2} - k_2 p_{\text{CO}}^2}{1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}}. \quad \dots\dots\dots (8)$$

This equation will express the condition of thermodynamic equilibrium, when the net rate of production of carbon monoxide is zero, that is,

$$\frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} = \frac{2k_1}{k_2} = K. \quad \dots\dots\dots (9)$$

Although the above systems will fit the individual experimental results at pressures of 1 atm and less, it was not known whether the same kinetic system will apply at higher pressures. The effect of carbon type was also not clearly understood nor its relationship to the mechanism of the reaction. For this reason it was decided to study the system carbon-carbon dioxide over a pressure range of 1 to 40 atm.

II. EXPERIMENTAL

(a) Apparatus

A flow system was used in which the reactant gases were allowed to flow through a heated carbon bed at known conditions of temperature, pressure, and flow rate. This apparatus is the same as that described by Blackwood and McGrory (1958).

Since carbon dioxide tended to freeze on expansion through control valves, these valves were modified by winding a heating element around the outside of the valve. For experiments in which hydrogen was present in the inlet gas, the evaporator and superheater were by-passed so that gases entered the bottom of the reactor vessel cold and were heated to bed temperature on passage through the silica chips at the bottom of the reactor tube. This was necessary in order to avoid the possibility of catalytic water-gas shift in the carbon dioxide/hydrogen mixture in the inlet gases.

Since the supply of carbon monoxide was limited and accurately known inlet gas compositions were required, premixed gases were made by introducing known pressures of the required gases into a storage cylinder and mixing them by mechanical agitation.

TABLE I
CHEMICAL COMPOSITION OF JARRAH CHARs

Temp. of Charring (°C)	Percentage Analysis on Dry Basis				Oxygen (%) liberated on Heating in N ₂ as :		Oxygen (%) after Reaction liberated on Heating in N ₂ as :	
	C	N ₂	H ₂	Ash	CO ₂	CO	CO ₂	CO
650	92.55	0.10	2.69	0.05	0.47	2.56	0.43	1.70
750	94.24	0.11	1.70	0.02	0.39	1.27	0.34	1.17
850	96.00	0.11	1.46	0.11	0.31	0.73	0.24	0.71
950	96.43	0.10	0.99	0.07	0.37	0.61	0.22	0.58
1050	97.48	0.09	0.68	0.06	0.22	0.41	0.23	0.44
1150	97.42	0.08	0.69	0.08	0.27	0.34	0.25	0.32

(b) Raw Materials

The carbon used in studies was prepared from coconut shell and was identical with the material used by Blackwood and McGrory (1958). For the experimental studies of the effect of carbon structure on the rate of reaction, a series of chars was prepared from *Eucalyptus marginata* (jarrah) by the method given by Blackwood (1959). The relevant chemical properties are shown in Table 1. All were sized -7 B.S. sieve +14 B.S. sieve.

Oxygen was determined by heating the samples in a stream of dry, oxygen-free nitrogen, at a temperature of about 1200 °C, and collecting the liberated oxides of carbon. Carbon dioxide was absorbed in "Sofnolite" and carbon monoxide, liberated at the same time, was passed over copper oxide at 270 °C and oxidized to carbon dioxide, absorbed in a similar manner, and weighed separately. Analyses for carbon, hydrogen, nitrogen, and ash were made by the standard methods. The carbon dioxide used in these experiments was obtained from a cylinder of commercial carbon dioxide which contained nitrogen as the main impurity. Carbon monoxide was prepared by reacting carbon dioxide with carbon at 900 °C, the product being approximately 95 per cent. carbon monoxide and containing only carbon dioxide and a small amount of nitrogen as impurities. This gas was compressed in cylinders to 75 atm and used for the subsequent experimental work.

(c) Procedure

Before making an experimental run, the apparatus was pressurized and tested for leaks. A weighed sample of carbon, sufficient to give a bed height of 100 mm, was placed in the reaction tube and the apparatus sealed. The reactor was then brought up to the predetermined operating temperature and, with the outlet valve closed, was brought to the required pressure using a premixed inlet gas mixture of known composition. The inlet and outlet valves were then adjusted so that the flow rate and pressure remained constant at their chosen values. The exit gas rate was measured by means of a recording wet test gas meter and the exit gas was sampled either over mercury or by means of hypodermic syringes.

(d) Gas Analysis

Analyses of both inlet and outlet gases were made using either a Bone and Wheeler gas analysis apparatus or a gas chromatograph with a silica gel column and hydrogen as the carrier gas. The latter method was found to be extremely useful when only small amounts of carbon monoxide were present in the outlet gas or when the change in composition between inlet and outlet was small.

III. EXPERIMENTAL CONDITIONS

As in the case of the carbon-steam reaction (Blackwood and McGrory 1958), it was necessary to choose experimental conditions such that the effects to be studied could easily be measured. For this reason a number of preliminary runs was made so that the gasification rate, measured as the number of gram moles of carbon monoxide formed per minute per gram of carbon, could be measured with reasonable accuracy over a known range of temperature and pressure. The following conditions were chosen.

(a) Space Velocity

A space velocity of 0.3 sec⁻¹ was used throughout this work. Gadsby *et al.* (1948) and Ergun (1955) have shown that at temperatures below 1000 °C the reaction is not diffusion-controlled and Blackwood and McGrory (1958) have shown that in the apparatus used temperature distribution should be satisfactory at space velocities below 2 sec⁻¹.

(b) *Bed Height*

A bed height of 100 mm was used for all runs since a uniform temperature could be maintained over this length of bed. Preliminary runs at 870 °C and 1 atm pressure showed that the rate of gasification was linearly related to the bed height, except for very short beds of less than 15 mm. The volume of the 100 mm bed was 17.6 c.c. and required a change of approximately 7.5 g of carbon.

(c) *Inlet Gas Composition*

A mole fraction of 0.9 was chosen for the inlet carbon dioxide at all pressures. The remaining 0.1 mole fraction was made up of nitrogen or nitrogen/carbon monoxide mixtures and at a given pressure the mole fraction of carbon monoxide could be set between the limits 0 to 0.1. Greater amounts of carbon monoxide, particularly at low temperatures, produced such a retarding effect that the analytical techniques were not sufficiently sensitive to measure accurately the change in carbon monoxide concentration.

(d) *Degree of Gasification*

In general, less than 10 per cent. carbon was gasified in any experiment and at low temperatures and pressures the amount was considerably less. The gasification rate at 870 °C and 20 atm of carbon dioxide was found to be effectively constant between 0 and 10 per cent. gasification and rates observed during this period can be considered as those at zero gasification.

(e) *Temperature*

For the kinetic studies three temperatures were chosen, namely 790, 830, and 870 °C. Over this temperature range the rate of reaction was measurable. For the study of the effect of char preparation, all runs, in which the chars made from *E. marginata* were used, were made at 650 °C, the lowest temperature of char preparation.

(f) *Total Pressure*

The total pressure in the kinetic study was varied over the range 5 to 40 atm. The upper pressure limit was set by the critical pressure of the inlet gas at the temperature in the supply cylinder. For the wood chars a pressure of 1.2 atm was used.

IV. RESULTS

A series of runs was made at each of the three temperatures in which the partial pressure of carbon monoxide at the inlet was varied while the carbon dioxide partial pressure was maintained constant. These runs were repeated at different partial pressures of carbon dioxide. The results are shown in Figure 1 and indicate that for a fixed partial pressure of carbon dioxide, the rate, as defined above, is approximately inversely proportional to the partial pressure of carbon monoxide. The points are experimental determinations and the curves are calculated from the rate equation (31) given later. In Figure 2, the rates are shown as a function of carbon dioxide partial pressure for constant carbon monoxide partial pressure. It can be seen that at high temperatures and low

carbon monoxide partial pressures, the rate is almost linearly related to the partial pressure of carbon dioxide. However, at lower temperatures and higher carbon monoxide partial pressures the rate increases with increasing carbon dioxide partial pressure to an exponent greater than unity.

Further runs were made in which carbon dioxide only was used in the inlet to the reactor. The results are shown in Figure 3, where it is seen that the apparent order of the reaction tends to zero at high pressures; and this has been shown (Gadsby *et al.* 1948) to be due to the retarding effect of the carbon monoxide produced during reaction.

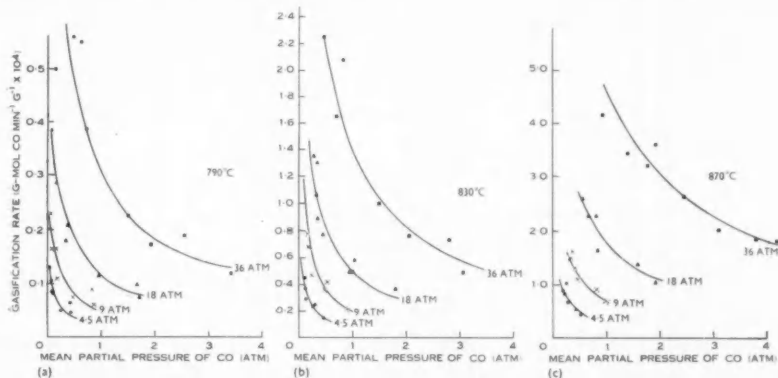


Fig. 1.—Relationship between gasification rate and mean CO partial pressure for the fixed partial pressures of CO₂.

● 4.5 atm, × 9 atm, ▲ 18 atm, ■ 36 atm. The points are experimental values and the curves are drawn for values calculated from equation (31).

It is known that hydrogen strongly inhibits the carbon-steam reaction just as carbon monoxide inhibits the carbon-carbon dioxide reaction. Long and Sykes (1948) suggested that this was due to competition for active sites by hydrogen. If this mechanism is correct then, if the same active sites are concerned, it would be expected that hydrogen would have a strong inhibiting effect on the carbon-carbon dioxide reaction and, in fact, these authors suggested that this is so. To test this theory, two experiments were made in which the inlet carbon dioxide contained, in one case, 0.1 mole fraction of hydrogen and in the other case, 0.1 mole fraction of nitrogen. The results of these experiments are shown in Table 2. It is clear from these results that there is no retarding effect due to hydrogen.

Since the carbon-carbon dioxide reaction is reversible, it was considered that some measurements of the velocity of the reverse reaction would help to clarify the mechanism. Experiments were made using carbon monoxide only as the inlet gas. The results of these experiments showed that the rate of production of carbon dioxide decreased rapidly as the time of reaction increased, and this appeared to be due to the deposition of carbon.

Experiments made with carbon monoxide flowing through the silica-packed reactor tube with no carbon present showed that the rate of production of carbon dioxide was approximately 60 times that obtained when carbon was present under the same conditions of temperature and pressure. This means that

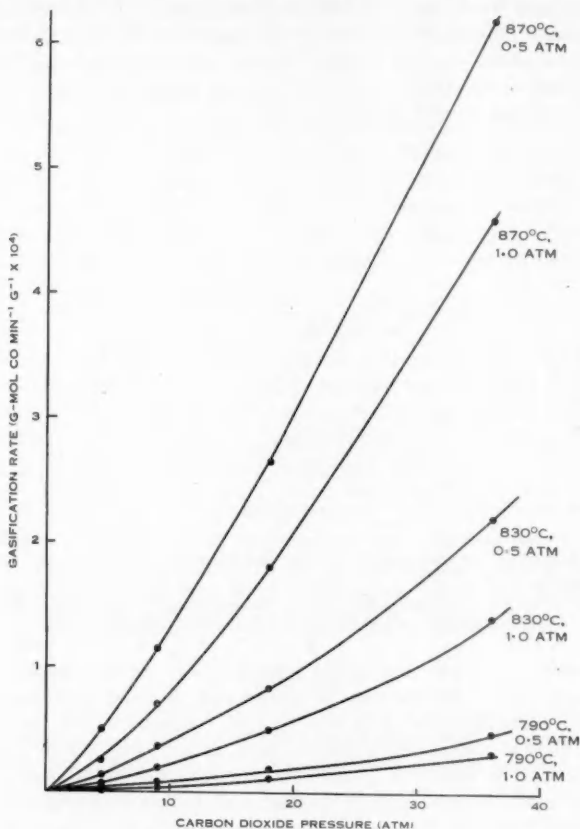


Fig. 2.—Variation of reaction rate with CO_2 partial pressure at constant CO partial pressures indicated.

carbon monoxide, converted in the lower part of the reactor over the silica to carbon dioxide, is reconverted to carbon monoxide in the bed so that the measurements give no indication of the true rate.

With this type of apparatus, measurements of rate when using gas mixtures near the theoretical equilibrium concentration are impracticable since the changes in concentration are so small that they cannot be measured with sufficient accuracy.

Chars prepared from *E. marginata* were reacted, with carbon dioxide only in the inlet, at a temperature of 650 °C and 1.2 atm pressure. The results are shown in Figure 4, where it is seen that there is a sharp decrease in reaction rate as the temperature of char preparation is increased from 650 to 950 °C, thereafter

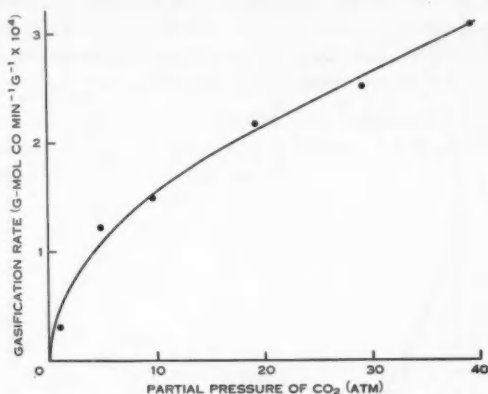


Fig. 3.—Variation of reaction at 830 °C with increasing pressure of CO₂ and no added CO in the inlet gas.

the rate tending to become more uniform. The oxygen contents of the chars both before and after reaction with carbon dioxide are also shown in Figure 4. Oxygen, as stated earlier, is liberated as both carbon monoxide and carbon dioxide on heating in a stream of nitrogen and the results show that the oxygen

TABLE 2
EFFECT OF HYDROGEN AND NITROGEN ON CARBON-CARBON DIOXIDE REACTION

Temperature (°C)	P_{CO_2} (atm)	P_{CO} (atm)	Rate (g-mol CO min ⁻¹ g ⁻¹ × 10 ⁻⁴)	
			0.1 Mole Fraction H ₂	0.1 Mole Fraction N ₂
830	18	0.34	1.3	1.08
830	9	0.23	1.07	0.80

liberated as carbon monoxide follows closely the reactivity curve for these chars to carbon dioxide. The amount of oxygen liberated as carbon dioxide is almost constant for all chars. The oxygen contents of the chars which have been reacted with carbon dioxide are lower than the initial figures but show the same type of variation.

V. DISCUSSION

(e) Interpretation of Kinetic Data

Since only a small proportion of the carbon dioxide was decomposed by reaction in the bed and the changes in partial pressure between inlet and outlet were small, the reactor can be considered as effectively differential in character. This was particularly so at high carbon monoxide partial pressures where the rate of reaction was so slow that changes in partial pressures of the reactants between inlet and outlet were less than 1 per cent.

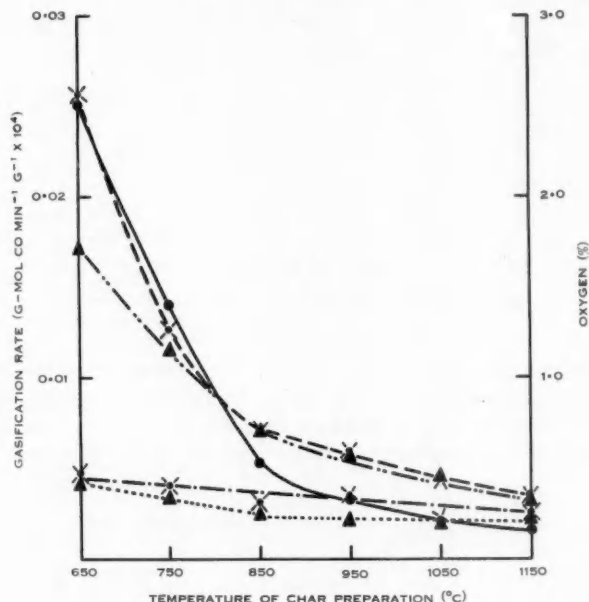


Fig. 4.—Relationship between reaction rate, oxygen content, and temperature of char preparation.

—•— Reaction rate at 650 °C and 1.2 atm CO_2 . Oxygen liberated as CO on heating in nitrogen: X—X before reaction, ▲—▲ after reaction. Oxygen liberated as CO_2 on heating in nitrogen: X—X before reaction, ▲—▲ after reaction.

Equation (5), proposed by Gadsby *et al.* (1948), has been shown to express the results at atmospheric pressure and it is of interest to present the high pressure data in a similar form. In Figure 5 the values of p_{CO_2}/R are plotted as a function of the mean p_{CO} . If equation (5) is to represent the results then a series of straight lines of constant slope and intercept increasing with increasing p_{CO} , should follow. Figure 5 shows that this is not the case and that the slope changes with changing p_{CO} .

The behaviour at atmospheric pressure has also been explained satisfactorily by equation (8) (Semechkova and Frank-Kamenetskii 1940). At atmospheric pressure and temperatures above 800 °C, the value of $k_8 p_{\text{CO}}^2$ are small enough to be ignored. However, at higher pressures where equilibrium tends to favour the formation of carbon dioxide, this term may be significant. Hence, on applying this equation to the results in Figure 5, it can be seen that the plots of p_{CO_2}/R v. p_{CO} should not be straight lines but curves, if the term $k_8 p_{\text{CO}}^2$ is significant. It also indicates that the curves will not intersect.

The equation (7) of Evropin, Kulkova, and Temkin (1956) does not fit the experimental results at high pressure and it is clear that some new system must be used to explain the change in kinetic behaviour.

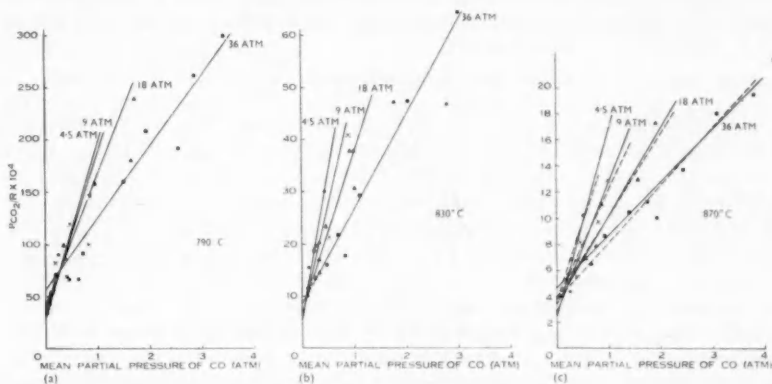
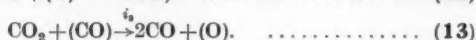
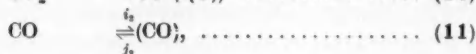


Fig. 5.—Relationship between p_{CO_2}/R and mean partial pressure of CO at the fixed pressures of CO_2 .

● 4.5 atm, × 9 atm, ▲ 18 atm, ■ 36 atm and temperatures (a) 790 °C, (b) 830 °C, (c) 970 °C. The dotted curves on (c) illustrate the concept of the common intercept.

Since the rate, at higher partial pressures of carbon monoxide, is greater than would be expected from equation (5), it appears that a mechanism is involved in which either the carbon monoxide is less effective as a retardant, or the amount of adsorbed oxygen is increased. It is possible that both of these effects could occur simultaneously. In the case of the carbon-steam reaction (Blackwood and McGrory 1958) a similar behaviour was explained on the assumption that hydrogen, adsorbed on the carbon surface, could react with steam to produce methane and adsorbed oxygen. The fact that methane was present in the product gas gave support to this theory. In the case of the carbon-carbon dioxide reaction such evidence is not available since the only product is carbon monoxide. However, if such a step be assumed, on an analogy with the carbon-

steam system, then the possible steps in a mechanism representing the gasification of carbon by carbon dioxide could be expressed as follows:



Although at high carbon dioxide partial pressures, production of carbon monoxide is favoured, as the temperature is decreased and the carbon dioxide pressure is increased, the equilibrium composition is more in favour of carbon dioxide. It is necessary, therefore, to consider a reverse mechanism by which carbon monoxide can be converted to carbon dioxide. Such a step has been suggested by Semechkova and Frank-Kamenetskii (1940) and by Reif (1952) and is represented by the following equation



As stated earlier, the retarding effect of carbon monoxide can be explained on the basis of a reversal of equation (10) and omission of equation (11). However, the presence of adsorbed carbon monoxide is necessary to explain the higher rates brought about through the reaction represented in equation (13) and to explain the reverse mechanism expressed by equation (14). Since the evidence for neglecting equation (11) in favour of the reverse of equation (10) is based on experiments at pressures of 1 atm or less and on the assumption that the same active sites are responsible for both steam and carbon dioxide decomposition, it may not be justifiable to make these assumptions at higher pressures and the evidence of change in reactivity to carbon dioxide with change in oxygen content of the chars indicates that perhaps, as Long and Sykes suggested (1948), the active centres are different in the case of the carbon-carbon dioxide reaction. Further, it has been stated by Semechkova and Frank-Kamenetskii (1940) that carbon monoxide is adsorbed on a carbon surface.

If the mechanism is represented by equations (10) to (14) and θ_1 and θ_2 are the fractions of the surface occupied by adsorbed oxygen and adsorbed carbon monoxide respectively, then, in the steady state, the equation expressing the balance of adsorbed oxygen, carbon monoxide, carbon dioxide, adsorbed carbon monoxide, and carbon are:

$$i_1 p_{\text{CO}_2} (1 - \theta_1 - \theta_2) + i_3 \theta_2 p_{\text{CO}_2} - i_4 \theta_1 = 0, \dots\dots\dots (15)$$

$$i_1 p_{\text{CO}_2} (1 - \theta_1 - \theta_2) + j_2 \theta_2 + 2i_3 \theta_2 p_{\text{CO}_2} + i_4 \theta_1 - i_2 p_{\text{CO}} (1 - \theta_1 - \theta_2) - j_5 \theta_2 p_{\text{CO}} = R, \dots\dots\dots (16)$$

$$i_1 p_{\text{CO}_2} (1 - \theta_1 - \theta_2) + i_3 \theta_2 p_{\text{CO}_2} - j_5 \theta_2 p_{\text{CO}} = \frac{1}{2} R, \dots\dots\dots (17)$$

$$i_2 p_{\text{CO}} (1 - \theta_1 - \theta_2) - j_2 \theta_2 p_{\text{CO}_2} - j_5 \theta_2 p_{\text{CO}} = 0, \dots\dots\dots (18)$$

$$i_4 \theta_1 - j_5 \theta_2 p_{\text{CO}} = \frac{1}{2} R, \dots\dots\dots (19)$$

where p_{CO_2} and p_{CO} are the partial pressures of carbon dioxide and carbon monoxide respectively and R is the net rate of formation of carbon monoxide.

Of equations (15) to (19) only three are independent so that elimination of θ_1 and θ_2 among three of them will lead to an expression for R in terms of p_{CO} and \bar{p}_{CO} and the various rate constants for the five reactions (10) to (14). This is given by

$$R = \frac{i_1 p_{CO_2} + (i_1 i_3 / j_2) p_{CO_2}^2 + (i_2 i_3 / j_2 + i_1 j_3 / j_2) p_{CO} p_{CO_2} - (i_2 j_3 / j_2) p_{CO}^2}{1 + (i_2 / j_2 + j_3 / j_2) p_{CO} + (i_1 / i_4 + i_2 / j_2) p_{CO_2} + (i_2 i_3 / i_4 j_2 + i_1 j_3 / i_4 j_2) p_{CO} p_{CO_2} + (i_1 i_3 / i_4 j_2) p_{CO_2}^2} \quad (20)$$

Equation (21) may be rewritten

$$R = \frac{k_1 p_{CO_2} + k_4 p_{CO} p_{CO_2} + k_5 p_{CO_2}^2 - k_8 p_{CO}^2}{1 + k_2 p_{CO} + k_3 p_{CO_2} + k_6 p_{CO} p_{CO_2} + k_7 p_{CO_2}^2}, \quad (21)$$

where the coefficients are replaced, for convenience, by the constants k_1 to k_8 .

Equation (21) is of suitable form to express the results qualitatively and with a suitable choice of constants can be made to give a reasonable fit to the experimental results.

Since the accumulation of sufficient data to enable a statistical method, such as least squares, to be used is impracticable, for reasons given earlier, a more reasonable approach is to examine the experimental data and, if possible, eliminate some of the constants by qualitative argument.

From Figure 5 it is seen that the experimental points on the plot of p_{CO_2}/R v. \bar{p}_{CO} lie approximately on straight lines and further, that these lines can be drawn, with a small loss of accuracy, to have a common intercept. Rearrangement of equation (21) gives

$$\frac{p_{CO_2}}{R} = \frac{1 + k_2 p_{CO} + k_3 p_{CO_2} + k_6 p_{CO} p_{CO_2} + k_7 p_{CO_2}^2}{k_1 + k_4 p_{CO} + k_5 p_{CO_2} - k_8 p_{CO}^2 / p_{CO_2}}, \quad (22)$$

and it follows that, if equation (22) is to describe the curves of Figure 5, the term $(k_4 p_{CO} - k_8 p_{CO}^2 / p_{CO_2})$ must be small compared to $(k_1 + k_5 p_{CO_2})$ over the range of temperatures and pressures studied. If this term is neglected, equation (22) can be rewritten

$$\frac{p_{CO_2}}{R} = \frac{1 + k_3 p_{CO_2} + k_7 p_{CO_2}^2}{k_1 + k_5 p_{CO_2}} + \frac{(k_2 + k_6 p_{CO_2}) p_{CO}}{k_1 + k_5 p_{CO_2}}. \quad (23)$$

Since the plots of p_{CO_2}/R v. \bar{p}_{CO} have been drawn to have a common intercept, the term

$$\frac{1 + k_3 p_{CO_2} + k_7 p_{CO_2}^2}{k_1 + k_5 p_{CO_2}}, \quad (24)$$

must be independent of p_{CO_2} and this implies that the term $k_7 p_{CO_2}^2$ must be small compared with $1 + k_3 p_{CO_2}$ and that for all values of p_{CO_2}

$$1 + k_3 p_{CO_2} \equiv \alpha (k_1 + k_5 p_{CO_2}), \quad (25)$$

where

$$\alpha = 1/k_1, \quad (26)$$

and

$$k_3 = k_5/k_1. \quad (27)$$

Now from equations (20) and (21), the following relationship can be deduced

$$k_6 = \frac{k_4}{k_1} \left(k_3 - \frac{k_5}{k_1} \right), \quad \dots \dots \dots (28)$$

and if the value of k_5 , obtained from equation (27), is substituted in equation (28), $k_6=0$. Equation (23) may now be written

$$\frac{p_{CO_2}}{R} = \frac{1}{k_1} + \frac{k_2 p_{CO}}{k_1 + k_5 p_{CO_2}} \quad \dots \dots \dots (29)$$

The value of k_1 can be determined since $1/k_1$ is the intercept of the p_{CO_2}/R v. \bar{p}_{CO} curves at $\bar{p}_{CO}=0$.

If now, the values of R/p_{CO_2} at constant \bar{p}_{CO} are plotted against p_{CO_2} , the intercept at $p_{CO_2}=0$ will be given by

$$I = \frac{k_1}{1 + k_2 p_{CO}} \quad \dots \dots \dots (30)$$

Since k_1 is known, a value for k_2 can be obtained. A further value for k_2 can be obtained by plotting the inverse of the slopes of the p_{CO_2}/R v. \bar{p}_{CO} lines as a function of p_{CO_2} . The intercept of this plot, at $p_{CO_2}=0$ is k_1/k_2 and the slope is $k_1 k_3/k_2$ which will then give a value for k_3 . Using equation (27) and the values for k_1 and k_3 obtained by those methods, a value for k_5 can be obtained.

Using this method, the experimental results indicate that, within the range of variables studied, the values of $k_4 p_{CO} p_{CO_2}$, $k_6 p_{CO} p_{CO_2}$, $k_7 p_{CO_2}^2$, and $k_8 p_{CO}^2$ are small enough to be ignored and the rate of reaction can be expressed as

$$R = \frac{k_1 p_{CO_2} + k_5 p_{CO_2}^2}{1 + k_2 p_{CO} + k_3 p_{CO_2}} \quad \dots \dots \dots (31)$$

The values of the constants obtained by the method given above, when substituted in the rate equation (31) give predicted rates which are approximately 20 per cent. too low at high carbon dioxide partial pressures. This is apparently due to the fact that it has been assumed that the plots of p_{CO_2}/R v. \bar{p}_{CO} at constant p_{CO} have a common intercept. A better fit to the experimental points is obtained if the intercept increases with increasing p_{CO} . The values of the intercepts and slopes of these plots are then given by

$$\text{Intercept} = \frac{1 + k_3 p_{CO_2}}{k_1 + k_5 p_{CO_2}} \quad \dots \dots \dots (32)$$

$$\text{Slope} = \frac{k_2 p_{CO}}{k_1 + k_5 p_{CO_2}} \quad \dots \dots \dots (33)$$

If values of the slopes and intercepts are used in these equations, values for the four constants can be obtained. It is found that the values obtained by this method, when substituted in equation (31), give predicted rates in good agreement with the experimental values. In Figure 3 the curves are calculated using constants obtained in this manner. The values of the constants are given in Table 3.

Figure 6 shows a plot of the logarithm of the rate constants against the inverse of the absolute temperature and it is seen that practically straight lines result. The constants k_2 and k_3 are sums of constants and their plots are not strictly justified. However, the terms j_3/j_2 in k_2 and i_3/j_2 in k_3 are probably small compared to i_2/j_2 and i_1/i_4 respectively. The constants k_1 and k_5 have energies of activation of 76 and 86 kcal mole⁻¹ respectively.

TABLE 3
NUMERICAL VALUES FOR CONSTANTS OF THE RATE EQUATION (31)

Temperature (°C)	k_1 (g-mol min ⁻¹ g ⁻¹ atm ⁻¹ × 10 ⁻⁴)	k_2 (atm ⁻¹)	k_3 (atm ⁻¹)	k_5 (g-mol min ⁻¹ g ⁻¹ atm ⁻² × 10 ⁻⁴)
790	0.052	13.7	0.23	0.004
830	0.23	17.1	0.17	0.02
870	0.65	12.7	0.31	0.07

Equation (21) becomes, when the net rate of formation of carbon monoxide is zero, and neglecting the term $k_4 p_{CO} p_{CO_2}$:

$$k_3 p_{CO}^2 = k_1 p_{CO_2} + k_5 p_{CO_2}^2 \quad (34)$$

At atmospheric pressure, or lower, when equilibrium is approached, the term $k_5 p_{CO_2}^2$ becomes small compared with $k_1 p_{CO_2}$, and we approach the relationship given by thermodynamic equilibrium, on the assumption that equation (1) is truly reversible. The results indicate generally that at higher pressures the system is not a simple reversible process.

(b) Active Centres

Since the mechanism of reaction of both carbon dioxide and steam with carbon is suggested as being controlled by the presence of certain active centres it is of interest to see if any information can be obtained as to the nature of these active centres and their role in the gasification process. The experiments made with wood chars have helped to throw some light on this problem. Figure 4 shows that as the temperature of preparation of the char is increased the rate of carbon dioxide formation decreases at first rapidly and then only slowly. Further, the portion of the oxygen content of these chars, which is evolved as carbon monoxide, also bears some relationship to the rate of reaction.

It has been shown that, during the hydrogenation of carbon with hydrogen (Blackwood 1959), a similar type of relationship exists between the reactivity and the oxygen content evolved as carbon monoxide on heating, and further, it has been suggested that the oxygen evolved as carbon monoxide may be related to certain chemical groupings in the carbon, such as semiquinone structures or benzpyran groups. Although this correlation is by no means perfect, other evidence led to the conclusion that these types of groups may have a considerable effect in deciding the reactivity of the carbon to hydrogen. However, in the case of hydrogen, it is observed that the reactivity reached a maximum for chars prepared at temperatures of about 700–800 °C. It was also observed

that the oxygen content tended to follow this trend and the best correlation between oxygen content and reactivity was obtained in terms of the oxygen remaining in the char after treatment with hydrogen. Initially there was a considerable decrease in oxygen content of the carbon, the amount lost being approximately constant in each case as was also the oxygen lost as carbon dioxide on heating. In the case of gasification with carbon dioxide a small proportion of oxygen is lost during gasification but the residual oxygen, which was evolved

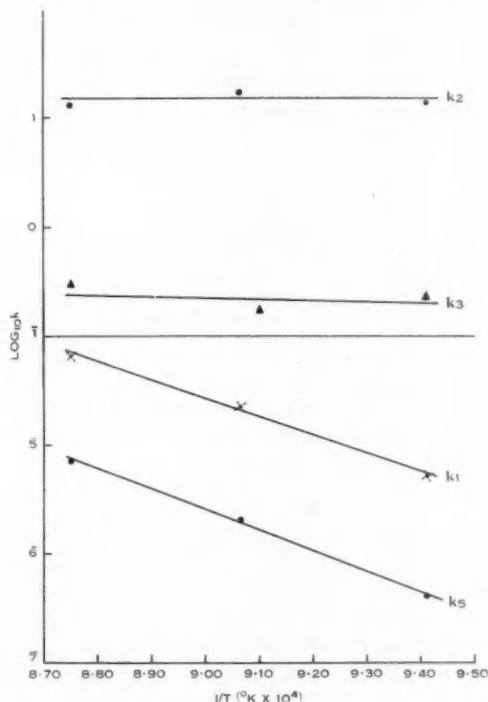


Fig. 6.—Plots of \log_{10} rate constants k_1 , k_2 , k_3 , and k_5 as a function of the inverse of the absolute temperature.

as carbon monoxide, was related very closely to the initial oxygen content evolved as carbon monoxide and no maximum was observed. This would indicate that other oxygen groups perhaps are present which may react with carbon dioxide, particularly in the lower temperature carbons but on reacting with hydrogen are destroyed in the process and take no further part. This could perhaps explain the statement of Long and Sykes (1948) that the active centres involved in the gasification of carbon with carbon dioxide might be different from those involved in the gasification with steam since it has also been observed (Blackwood and McTaggart 1959) that reactivity towards water vapour shows a maximum for

carbons prepared in the range 700–800 °C. Although it is clear that there is a relationship between the oxygen content of the chars and the reactivity, as shown in Figure 4, the estimation of chromene or benzopyran groups as described by Garten and Weiss (1957), indicates that in this case there is no satisfactory relationship between the acid absorptive properties of the carbon and the reactivity to carbon dioxide although reactivity to hydrogen did suggest that there might be some relationship between these properties. Since the chars used in this study were prepared from the same type of timber as those used for the study of hydrogenation (Blackwood 1959) by the same method under the same conditions, it would be expected that the properties of the carbons would be comparable. However, analysis shows that the carbons used in this study have generally a lower oxygen content for the higher temperature chars than was obtained previously and that their reactivities are lower than was found for the other chars. From the figures given in Table 1 it can be shown that the hydrogen/oxygen ratio for the samples, calculated on an equivalent basis, shows a maximum in the range 750–850 °C and indicates that the hydrogen may possibly be associated with the oxygen groupings and that the possibility of the presence of semiquinone structures as described by Garten and Weiss (1955) cannot be ignored.

VI. ACKNOWLEDGMENTS

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THE SORPTION OF OXYGEN BY SILVER

By J. A. ALLEN*

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Summary

The Gibbs adsorption equation has been used in conjunction with surface tension measurements on silver wires to determine the adsorption isobar of oxygen on silver at a pressure of 16 cmHg over the temperature range 650–850 °C. The results show the existence of a surface concentration of oxygen of 2×10^{15} atoms oxygen per cm².

The value of ΔH for the equilibrium between adsorbed and dissolved oxygen has been estimated as 20.6 kcal. This value in conjunction with the heats of formation and solution of Ag₂O in silver permit the heat of adsorption to be determined as 10.5 kcal per g-atom of oxygen.

I. INTRODUCTION

Solid silver in the presence of oxygen is extensively used as an oxidation catalyst. The appearance of such catalysts after use, for example, in the vapour phase oxidation of methanol to formaldehyde, indicates that considerable solution of oxygen in the metal has taken place. Attention is therefore directed to the relationships between the dissolved and adsorbed oxygen as a contribution to the study of the catalytic mechanism.

Data on the solubility of oxygen in solid silver due to Steacie and Johnson (1926) are available, but there exists little pertinent information on the adsorption of oxygen on silver at elevated temperatures, 600–900 °C. The experimental procedures normally employed in adsorption studies at low temperatures become rather intractable at elevated temperatures and a different approach has therefore been employed. This follows, in part, the work of Buttner, Fink, and Udin (1952) and involves the use of the Gibbs adsorption equation in conjunction with measurements of the surface tension of silver in a controlled oxygen environment.

II. THE SOLUTION OF OXYGEN IN SILVER

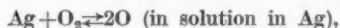
Steacie and Johnson (1926) have shown that the solution of oxygen in solid silver follows Sieverts' law and have established solution isobars for the temperature range 200–800 °C for pressures between 10 and 80 cmHg. A characteristic is the pronounced minimum in the isobars at about 400 °C and the rapid increase in solubility with increasing temperature above this value. At a pressure of 16 cmHg the values obtained by interpolation and extrapolation are shown in Table 1.

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TABLE 1
SOLUBILITY OF OXYGEN IN SILVER
Partial pressure 16 cmHg

<i>t</i> (°C)	600	630	660	690	720	750	780	810	840
cm ³ at S.T.P. per cm ³ Ag	0.059	0.065	0.073	0.082	0.094	0.111	0.137	0.170	0.212

Because Sieverts' law is obeyed the possibility that the oxygen is dissolved in the molecular form may be eliminated. For the process



the equilibrium constants K_1 and K_2 corresponding to the solubilities S_1 and S_2 at temperatures T_1 and T_2 should be related by the equation

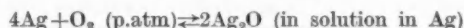
$$\ln \left(\frac{K_1}{K_2} \right) = 2 \ln \left(\frac{S_1}{S_2} \right) = - \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right), \dots \dots \dots (1)$$

where ΔH is the heat of solution per mole assumed constant for the temperature range T_1 to T_2 . The values of ΔH per g-atom were calculated from the data in Table 1 for successive intervals of 30 °C and expressed as a function of the mean temperature of the interval by a linear equation fitted by the method of least squares,

$$\Delta H_1 = -56.2 + 0.0678T, \dots \dots \dots (2)$$

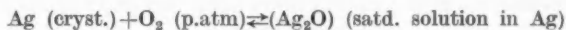
where ΔH_1 is in kcal per g-atom and T in °K.

This formulation does not distinguish solution of oxygen as atoms from solution as Ag_2O since if the equation is written



K_1/K_2 will also be equal to $(S_1/S_2)^2$.

Heats of solution obtained from solubility data are limiting values for solution in a solvent that differs only infinitesimally from saturation. The approximation made in identifying this with



should be noted. The values obtained will be comparable with those for the decomposition of Ag_2O for here the two solid species will be Ag saturated with oxygen at the equilibrium pressure and Ag_2O probably with the maximum permissible excess of Ag.

The very high value of ΔC_p of 67.8 cal deg⁻¹ associated with equation (2) raises the question of the interpretation of Steacie and Johnson's (1926) data. In the temperature range 600–900 °C and at subatmospheric pressures Ag_2O is thermodynamically unstable, the dissociation pressure at 400 °C, for example, being about 115 atm. Simons (1932) suggested that the Ag_2O was stabilized

by solution in silver and that the characteristics of the solubility isobars of oxygen in silver resulted from the operation of two factors, the increase in solubility of Ag_2O with temperature and the increase in the dissociation pressure with temperature. He has calculated from the data of Steacie and Johnson (1926) the solubility of Ag_2O in silver at various temperatures at the corresponding dissociation pressures of the oxide.

For the temperature range 600–923 °C the data so obtained yield a heat of solution of 16.8 kcal per g-atom of oxygen.

III. THE ADSORPTION OF OXYGEN ON SILVER

(a) Theoretical

For solid silver in contact with oxygen at pressure p and temperature T the surface excess of the solute Γ is given by the Gibbs equation

$$\Gamma = -\frac{c}{RT} \left(\frac{\partial \gamma}{\partial c} \right)_T, \quad \dots \quad (3)$$

where c is the concentration of the solute and γ the surface tension. Since Sieverts' law is obeyed

$$c = k_1 p^{1/2}, \quad \dots \quad (4)$$

and (3) becomes

$$\Gamma = -\frac{2}{RT} \left(\frac{\partial \gamma}{\partial \ln p} \right)_T, \quad \dots \quad (5)$$

Γ may therefore be calculated if γ is known as a function of p at constant temperature. This was the procedure adopted by Buttner, Fink, and Udin (1952).

Alternatively, since, for a saturated solution at constant pressure, γ will be a function of c and T only,

$$\left(\frac{\partial \gamma}{\partial T} \right)_p = \left(\frac{\partial \gamma}{\partial c} \right)_T \left(\frac{\partial c}{\partial T} \right)_p + \left(\frac{\partial \gamma}{\partial T} \right)_c, \quad \dots \quad (6)$$

and measurements of $(\partial \gamma / \partial T)_p$ and $(\partial \gamma / \partial T)_c$ together with a knowledge of $(\partial c / \partial T)_p$ permit Γ to be calculated. This approach has been used in the present work.

If, as will be shown, $(\partial \gamma / \partial T)_p - (\partial \gamma / \partial T)_c$ is constant over the temperature range of interest

$$\Gamma = \frac{c}{RT} k_2 \left(\frac{\partial c}{\partial T} \right)_p^{-1}, \quad \dots \quad (7)$$

where k_2 is a constant.

The "equilibrium" at constant temperature and pressure between oxygen in the bulk phase and in the surface layer may be written

$$\begin{aligned} K &= \frac{\text{concentration in surface layer}}{\text{concentration in bulk phase}} \\ &= \frac{1}{\tau RT} k_2 \left(\frac{\partial c}{\partial T} \right)_p^{-1}, \quad \dots \quad (8) \end{aligned}$$

K is therefore proportional to $\{T(\partial c/\partial T)_p\}^{-1}$ if τ , the thickness of the surface layer, is assumed constant. $\Delta \bar{H}$ for the "equilibrium" may be determined from the temperature coefficient of $\{T(\partial c/\partial T)_p\}^{-1}$. This is an oversimplification since the equilibrium is strictly between the total molecules in the surface layer and those in the bulk of solution. Formally, it means for a constant τ that Γ is directly proportional to c . In general, this is not so since $(\partial \gamma/\partial c)_T$ usually varies with c .

It may be noted that the above discussion is independent of the nature of the solutes provided that the solutes in solution and at the surface are of the same species.

(b) Experimental

The experimental procedure differed only in detail from that described by Buttner, Fink, and Udin (1952). The wires were drawn from 99.99 per cent. silver and had a radius, r , of 0.00535 cm. Lengths of 2.5–3 cm were used. The number of grains per cm, n/l , was 90 ± 10 and the surface tension was calculated from the equation

$$w = \pi r \gamma \left[1 - \frac{n}{l} \frac{r}{3} \right], \quad \dots \dots \dots (9)$$

where w is the load at zero strain.

Two series of measurements were carried out:

Series I—in air at a pressure of 1 atm over the temperature range 650–850 °C.

Series II—in mixtures of air and oxygen under the following conditions:

Partial pressure of oxygen			
(cmHg)	16	40	76
Temperature (°C)	790*	710	636

These pressures and temperatures were chosen in order to maintain c constant at 0.15 cm³ per cm³ Ag based on the solubility data of Steacie and Johnson (1926).

(c) Results

The results of Series I are shown in Figure 1. Three values of γ measured at the same pressure by Buttner, Fink, and Udin (1952) are also shown. The equation to the straight line fitted by the method of least squares is

$$\gamma (p=16 \text{ cmHg}) = 2050 - 1.71t, \quad \dots \dots \dots (10)$$

where γ is in dynes per cm and t in °C.

The results of Series II are shown in Figure 2. The equation to the straight line fitted by the method of least squares is

$$\gamma (c=0.15 \text{ cm}^3 \text{ per cm}^3 \text{ Ag}) = 1210 - 0.63t, \quad \dots \dots \dots (11)$$

where γ is in dynes per cm and t in °C.

* From Series I.

Substitution in equation (6) yields

$$\left(\frac{\partial \gamma}{\partial c}\right)_T = -1.08 \left(\frac{\partial c}{\partial T}\right)_p^{-1} \dots \dots \dots (12)$$

From the data in Table 1 $-\log_{10} \{T(\partial c/\partial T)_p\}$ computed for successive intervals of 30 °C is plotted in Figure 3 against $1/T$ where T is the mean temperature in °K for the interval. The equation to the line fitted by the method of least squares is

$$-\log_{10} \{T(\partial c/\partial T)_p\} = -4.24 + (4.47 \times 10^{-3})/T, \dots \dots (13)$$

whence $\Delta H_s = -20.6$ kcal.

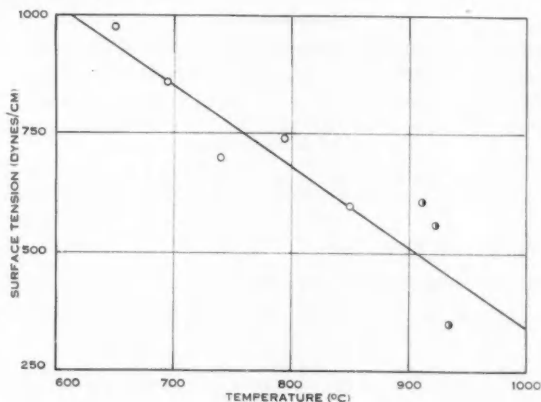


Fig. 1.—Surface tension of silver in air at 1 atm as a function of the temperature. ● Buttner, Fink, and Udin (1952).

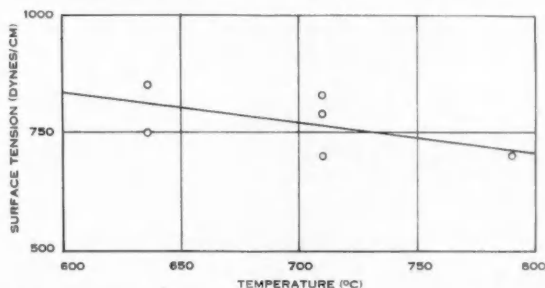


Fig. 2.—Surface tension of silver at a constant concentration of dissolved oxygen at 0.15 cm³ S.T.P. per cm³ Ag as a function of the temperature.

Substitution of the values of $(\partial \gamma/\partial c)_T$ calculated from (12) in (3) yields Γ as a function of the temperature. The results are shown in Figure 4. A single value of Γ for the same pressure but at a higher temperature determined by Buttner, Fink, and Udin (1952) from equation (5) is also plotted.

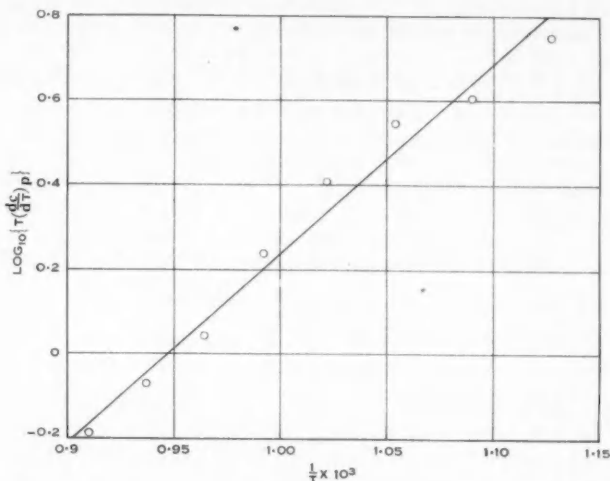


Fig. 3.—Logarithm of the constant for the equilibrium between dissolved and adsorbed oxygen as a function of the reciprocal of the temperature.

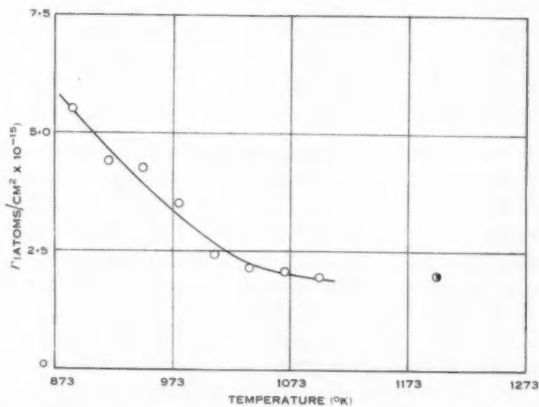
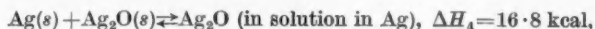


Fig. 4.—Surface concentration of oxygen on silver at a partial pressure of oxygen of 16 cmHg as a function of the temperature.

● Buttner, Fink, and Udin (1952).

The results in Section II may be combined with those in Section III to yield an estimate of the heat of adsorption. Because of the large temperature coefficient in the heat of solution, equation (2), which would be reflected in a similar coefficient in the heat of adsorption, the value of 16.8 kcal per g-atom of oxygen obtained from Simons' (1932) treatment of Steacie and Johnson's

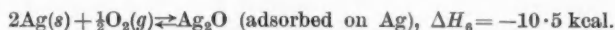
(1926) data is preferred. In this case Ag_2O is nominally the solute and the following equations may be written:



Ag_2O (in solution in Ag) $\rightleftharpoons \text{Ag}_2\text{O}$ (adsorbed on Ag), $\Delta H_5 = -20.6 \text{ kcal}$,
and from the heat of formation of $\text{Ag}_2\text{O}(s)$ in the range 600–900 °C,



By addition



The heat of adsorption in this case is therefore 10.5 kcal per g-atom of oxygen over the temperature range.

IV. DISCUSSION

It is evident from Figures 1 and 4 that in so far as the present results may be compared with those of Buttner, Fink, and Udin (1952) the agreement is satisfactory. The value of Γ at the upper end of the temperature range, $\sim 2 \times 10^{15}$ atoms per cm^2 may be compared with the maximum number of oxygen atoms per cm^2 that could occupy sites on the main crystal faces of silver and with the number per cm^2 in the various planes of Ag_2O . The figures are as follows:

	Crystal Plane	No. Oxygen Atoms $\times 10^{-15}$		Crystal Plane	No. Oxygen Atoms $\times 10^{-15}$
Ag	(100)	1.2	Ag_2O	(100)	0.45
	(110)	0.85		(110)	0.65
	(111)	1.4		(111)	0.80

The values for the planes of silver are probably an overestimate since it is unlikely that every potential site could simultaneously be occupied. It may be noted that Buttner, Fink, and Udin (1952) found that at 932 °C Γ did not vary with pressure over the range 0.0001–0.2 atm.

The higher values of Γ obtained at the lower temperatures may not be genuine. The accuracy with which measurements of the surface tension can be made renders it unrealistic to fit other than straight lines to the data in Figures 1 and 2. k_2 , the difference between $(\partial\gamma/\partial T)_p$ and $(\partial\gamma/\partial T)_c$, on which Γ depends, is constant because of these impositions of linearity. Modest departures from linearity with temperature of either or both of these coefficients could introduce a change in k_2 by the necessary factor of 2 or 3. If the increased value of Γ at lower temperatures were genuine this could be interpreted as indicating considerable stability of a surface layer, approximating to silver oxide. This appears unlikely. The assumption of a constant thickness τ of the surface layer would also become invalid. A further possibility is that the increased values of Γ arise because equilibrium between dissolved and adsorbed oxygen has not been established at the lower temperatures.

The heat of adsorption of 10.5 kcal per g-atom of oxygen is about the value to be expected, being of the same order but somewhat greater than the heat of

formation of the oxide. It depends, however, on the value used for the heat of solution which is by no means free of doubt and on that for the enthalpy change associated with the equilibrium between oxygen in the surface layer and in the bulk of the solution which has been estimated by a method lacking in strict validity.

The results as a whole do not yield specific information on the nature of oxygen adsorbed or dissolved in solid silver at the temperatures in question. The use of the Gibbs equation involves the assumption that the species in the solution is the same as that at the surface. In computing the heat of adsorption the thermochemical formulation treats the solute as a molecular entity Ag_2O , whereas the dissolved oxide would be expected to be dissociated in solution.

V. CONCLUSION

The present work demonstrates that not unreasonable results on the adsorption of oxygen on silver at elevated temperatures can be obtained from surface tension measurements. In the temperature range 600–900 °C in contact with oxygen at a pressure of 16 cmHg, it is evident that the adsorbed layer in equilibrium with dissolved oxygen and with the gaseous phase has an oxygen content of at least 2×10^{15} atoms of oxygen per cm^2 . The heat of adsorption, 10.5 kcal per g-atom, should be considered only as an estimate. The high stable concentration of oxygen at the gas/solid interface is apparently a significant factor in the functioning of the silver/oxygen system as an oxidation catalyst.

VI. ACKNOWLEDGMENTS

The author is indebted to Professor A. E. Alexander, University of Sydney, for a useful discussion. The work was carried out, in part, in the Central Research Laboratories, Imperial Chemical Industries of Australia & New Zealand Limited.

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INTRAMOLECULAR VAN DER WAALS-LONDON COHESIONS AND CHEMICAL REACTIVITY: THE TRANSITION STATE IN THE BIMOLECULAR NUCLEOPHILIC DISPLACEMENT REACTION OF HALIDE ION WITH ALKYL HALIDE

By E. SPINNER*

[Manuscript received September 17, 1959]

Summary

The intramolecular London-van der Waals cohesions in the transition states $\text{Hal}^{\text{b}} \cdots \text{CH}_3 \cdots \text{Hal}^{\text{b}}$ in which both halogen atoms are identical should be greater than the following: $\text{Hal}=\text{F}$, 0.09; $\text{Hal}=\text{Cl}$, 0.6₄; $\text{Hal}=\text{Br}$, 0.9₄; $\text{Hal}=\text{I}$, 1.1₄ kcal/mole. It is concluded that these cohesions make a significant contribution to the observed increase in the velocity of the above displacement reaction as the polarizability of either entering or leaving halogen atom increases.

I. INTRODUCTION

London-van der Waals attractive forces (London 1937) are known to operate within molecules (Eyring 1932). They increase as the polarizabilities of the units attracting one another increase and can be expected to be prominent in molecules containing several multiple bonds (Simpson 1951; Spinner 1957) or several atoms of high atomic number. The attraction tends to be greater between identical and regularly arranged units than between dissimilar and irregularly arranged ones. London-van der Waals cohesions play a part even in molecules composed of constituents of low polarizability such as paraffins (Pitzer and Catalano 1956). They explain why the apparent C-H bond energy is higher in methane (by ~ 1.4 kcal/mole) (Mulliken, Rieke, and Brown 1941) than it is in other hydrocarbons; why the apparent C-C bond energy in diamond is higher (by ~ 1 kcal/mole) (Mulliken, Rieke, and Brown 1941) than it is in paraffins. These cohesions contribute to the total binding in halogen molecules (Pitzer 1955), and explain why the ion I_3^- is more stable than Br_3^- , while the ion Cl_3^- does not appear to exist.

The difference in intramolecular London-van der Waals cohesions, as between products and reactants, or between transition state and reactants, is one of the factors affecting the energetics of every chemical change (Spinner 1956). Recently Bunnett (1957) and Reinheimer and Bunnett (1959) have found that certain nucleophilic substitution reactions are facilitated by a high polarizability in either reactant; they showed that their observations cannot be explained satisfactorily except in terms of London-van der Waals attraction.

II. METHOD OF CALCULATION

Most transition states are too complicated to permit even rough estimates of the van der Waals-London cohesions within them. However, the transition

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state obtained in the bimolecular nucleophilic displacement reaction between halide ion and methyl halide,* $\text{Hal}^{1-} \dots \text{CH}_3 \dots \text{Hal}^{1-}$, is comparatively simple, if the entering and leaving halogen atoms are identical. Though a calculation of the *total* cohesion energies is hardly practicable even here, the major cohesion energy (which represents a *lower limit* for the total cohesion) may be estimated. The most important cohesions present in the transition state, and absent from the initial state, are those between the incipient $\text{C} \dots \text{Hal}$ bonds. These are linearly arranged, and London's formula (1) for the van der Waals-London cohesion energy, U_0 (London 1937), is the most suitable one for dealing with such a symmetrical system of two identical units.

$$U_0 = -\frac{3}{4} h \nu_0 \alpha^2 / R^6, \quad \dots \dots \dots (1)$$

where h is Planck's constant, α is the polarizability of each unit, ν_0 is the frequency of the electron oscillation giving rise to the most intense electronic transition (in the isolated unit), and R is the distance between the units.

The following approximations will be made in this treatment :

(i) $h\nu_0$ will be taken to be the ionization potential of the halogen atom in the corresponding methyl halide (cf. London 1937).

(ii) α will be taken to be one-quarter of the normal polarizability of the halogen atom in organic compounds (the total polarizability being supposed to be due to the eight outer halogen electrons). This is an underestimate, very considerably so in the case of fluorine ; strictly, one ought to add between one-sixteenth and one-quarter of the polarizability of carbon.*

(iii) R will be taken to be the distance between the centres of the incipient bonds, that is, the $\text{C} \dots \text{Hal}$ internuclear separation. The halogen bond radius in the transition state is assumed to be the mean of the ionic and the normal covalent bond radii, the carbon bond radius is assumed to have its normal value of 0.77 Å. R is probably underestimated here for the highly polar $\text{C} \dots \text{F}$ bond, but almost certainly overestimated for the $\text{C} \dots \text{I}$ bond, in which the bonding electrons should be closer to the C than to the I nucleus.

(iv) Two approximations are implicit in the use of equation (1) : (a) equation (1) holds accurately only for truly harmonic electron oscillations ; polar units represent anharmonic (asymmetric) oscillators ; however, no means for estimating the anharmonicity corrections are available ; (b) the attraction between two identical coaxial dipoles is proportional not to $1/R^3$ but to $1/R(R^2 - z^2)$, where z is the separation of charges within each dipole ; thus, for the longitudinal electron oscillations, which account for $\frac{2}{3}$ of U_0 according to (1), R^6 should be replaced by $R^2(R^2 - \bar{z}^2)^2$, where \bar{z} is a suitably weighted mean oscillation amplitude of the electrons (see Appendix I) ; this means that for small values of R equation (1) leads to U_0 values that are too low.

Approximations (i) and (ii) imply an effective neglect of anisotropy ; (i) and, for the lower halogen atoms, (iii) lead to overestimates of U_0 , but these are more

* Only one electron pair is assigned to each incipient bond. Atomic refractions are so defined that to obtain the molecular refraction of, say, carbon tetrachloride, one has to add the atomic refraction of carbon to four times the atomic refraction of chlorine, which gives one atomic refraction of chlorine + $\frac{1}{4}$ atomic refraction of carbon per $\text{C}-\text{Cl}$ unit.

than compensated for by the considerable underestimates of U_0 arising from approximation (iv (b)) and, for the lower halogen atoms, from (ii). The values of U_0 thus calculated therefore represent a lower limit for the cohesion between the two incipient C . . . Hal bonds. The non-bonding halogen electrons give rise to additional cohesions which must amount to an appreciable fraction of U_0 . There is also some attraction between the halogen atoms and the CH bonds, but this may be more than offset by steric repulsions (especially in the transition states of the higher alkyl halides Hal . . . CHR . . . Hal).

TABLE I
INTRAMOLECULAR Hal . . . C/C . . . Hal COHESION ENERGIES IN THE TRANSITION STATES
Hal . . . Me . . . Hal, AND DATA* USED IN THEIR CALCULATION

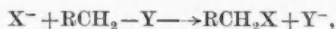
Halogen	F	Cl	Br	I
r (Hal) (Å)	0.64	0.99	1.14	1.33
r (Hal ⁻) (Å)	1.36	1.81	1.96	2.19
r (C . . . Hal ^{1/2}) (Å)	1.77	2.17	2.32	2.53
$I.P.$ (M Hal) (eV)	~13†	11.2	11.2	9.5
$[R]$ (Hal) (c.c./g.-atom)	1.088	5.933	8.803	13.76
U_0 (kcal/mole)	~0.09	0.6 ₄	0.9 ₄	1.1 ₅

* Ionic and bond radii, r , Glasstone (1940); ionization potentials, $I.P.$, Price (1947); atomic refractions for the α -hydrogen line, $[R]$, Ingold (1953, p. 121).

† Estimate (the true value is unknown).

III. RESULTS AND CONCLUSIONS

Table 1 gives the experimental values used in the calculations.* From the U_0 values in Table 1 it is clear that London-van der Waals stabilization of the activated complex containing two fluorine atoms is almost negligible, but when halogen atoms of higher polarizability are present it becomes quite appreciable. It has long been known that the velocity of the bimolecular nucleophilic replacement reaction



increases with increasing polarizability of both X and Y. Normally this is attributed to (i) increasing ion-dipole interaction as the polarizability of X^- increases, and (ii) the greater facility of C—Y bond fission with atoms Y in which the outer electrons are less firmly held. There is no doubt that these effects, especially (ii), are important, but it is clear that van der Waals-London attraction contributes significantly to the observed order of reactivity, not only in the methyl halides, for which the U_0 values in Table 1 represent considerable underestimates of the attraction, but also in higher alkyl halides, for which the U_0

* The polarizability per outer electron pair, used as α in equation (1), is obtained by the relation

$$\alpha = \frac{1}{4} \times \frac{3}{4\pi} \times \frac{[R]}{N},$$

where N is Avogadro's number.

values are probably only slight underestimates. The total activation energies of these reactions are in the vicinity of 16 kcal/mole for methyl bromide and iodide, and 17.5 to 20 kcal/mole for the higher alkyl compounds (Ingold 1953, p. 408, where these reactions are discussed in detail).

IV. ACKNOWLEDGMENT

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APPENDIX I

The Effect of Finite Dipole Length on London-van der Waals Attraction

If the length of the oscillating dipoles is no longer negligible compared with the distance between them, the favourable dispositions of dipoles $+- + -$ will be energetically preferred over the unfavourable ones $+- -+$ to an even greater extent than the simple London treatment requires. In terms of the dynamics of the electron motions, in the in-phase mode of oscillation the electrons will move more slowly (especially when in the extreme positions) than they do in the case of negligibly short dipoles. Conversely, in the out-of-phase mode the electrons will move correspondingly more rapidly (especially when in the extreme positions) than they do in the simple case.

Thus London's (1937) formula for the frequencies of the longitudinal electron oscillations, $\nu = \nu_0 \sqrt{[1 \pm 2\alpha/R^2]}$, has to be replaced by one that takes into account the lowering of the in-phase, and the raising of the out-of-phase, oscillation frequency. The coefficient of London interaction varies with time;* the coefficient at any instant is given by $2\alpha/R(R^2 - z^2)$, where z is the length of the dipole at that instant. The average coefficient, to be used in the formula giving the "zero-order" frequencies, is $2\alpha/R(R^2 - \bar{z}^2)$, where \bar{z} is a suitably weighted mean length of the oscillating dipole (\equiv the suitably weighted mean oscillation amplitude of the electrons concerned).

* As a subsidiary effect of this, the electron motions will no longer be truly simple harmonic, even if they were so originally.

SOME STUDIES IN INORGANIC COMPLEXES

VII. COPPER(II) WITH 2-PICOLYLAMINE

By G. J. SUTTON*

[Manuscript received January 5, 1960]

Summary

A study has been made of the bis(2-picolylamine) copper(II) complex in association with various anions. Of the salts investigated, the chloride, bromide, and nitrate are blue, the iodide is green, and the perchlorate and tetraiodomercurate are purple. Blue solutions are obtained in water, and the molecular absorption spectra are identical and are characteristic of bispicolylamine copper(II) ion. However, conductance measurements in methanol and nitromethane show that there is some metal halogen bonding for the iodide, and this is also indicated by a slight shift in the absorption spectrum to longer wavelengths in the same solvents. The mean magnetic moment of the copper atom in the complexes was found to be 1.93 B.M.

I. INTRODUCTION

The violet-blue chelate bis(2-picolylamine) copper(II) ion is formed instantaneously in aqueous solution by allowing the base to react with copper salt. On shaking and allowing to stand, the complexes are precipitated as crystalline plates even in the case of the nitrate, at semimolar concentration. The salts are less soluble than the corresponding ethylenediamine complexes and the purple perchlorate and tetraiodomercurate may be of analytical value. The chloride, bromide, and nitrate are bright blue, whilst the iodide is green. With the exception of the very insoluble tetraiodomercurate, the salts at millimolar concentration in water give an identical blue colour and absorption spectra (Table 1), and conductances in water show that under these conditions the anions are free (Table 2). However, since the iodide only was found to be sparingly soluble in methanol and nitromethane, it was decided to carry out conductance measurements and measurements of absorption spectra in the visible spectrum in these solvents. Even at the necessarily low concentrations ($4 \times 10^{-4}M$), there is incomplete ionization of halogen (Table 2) and a shift of absorption to longer wavelength (Table 1). Although X-ray information is not available, the results indicate that an octahedral arrangement may exist in the solid state for the iodide. This has also been proposed by Figgis and Harris (1959) for an analogous copper(II) bromide complex of *o*-phenanthroline. It is interesting to observe that when the complex cation is coupled with perchlorate or tetraiodomercurate anions the salts are purple in colour. Since it is unlikely that any coordination by the anions takes place, the cation is probably a tetravalent

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square complex which can be octahedral in aqueous solution by solvent molecules. It is also noteworthy that none of the complexes investigated contains water molecules in the crystal state. Magnetic measurements were carried out, since Ray and Sen (1948) observed that red-yellow copper(II) complexes have a magnetic moment of 1.7-1.9 B.M., whilst those which are green-blue have moments of 1.9-2.0 B.M. It was found that even with the magnetically dilute

TABLE 1
ABSORPTION SPECTRA OF COPPER(II) COMPLEXES AT $2.00 \times 10^{-4}M$

Substance	Maxima	Minima	Solvent
Cu pic ₂ ⁺	595	450	Water
Cu pic ₂ I ₂	595	450	Water
Cu pic ₂ I ₂	610	475	Methanol
Cu pic ₂ I ₂	615	475	Nitromethane

TABLE 2
MOLECULAR CONDUCTANCES OF COPPER(II) COMPLEXES AT $10^{-3}M$ AT 25 °C

Substance	Ω^{-1}	Solvent	Substance	Ω^{-1}	Solvent
Cu pic ₂ Cl ₂ ..	258	Water	Cu pic ₂ I ₂ ..	216	Water
Cu pic ₂ Br ₂ ..	239	Water	Cu pic ₂ I ₂ ..	73	Methanol*
Cu pic ₂ (NO ₃) ₂ ..	242	Water	Cu pic ₂ I ₂	36.9	Nitromethane*

* $4 \times 10^{-4}M$ concentration.

TABLE 3
MAGNETIC SUSCEPTIBILITIES OF COPPER(II) COMPLEXES CORRECTED TO 20 °C

Substance	$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	$\chi_M \times 10^{-6}$	μ (B.M.)
Cu pic ₂ Cl ₂	4.18	1465	1587	1.94
Cu pic ₂ Br ₂	3.26	1435	1578	1.93
Cu pic ₂ I ₂	2.56	1368	1551	1.92
Cu pic ₂ (NO ₃) ₂ ..	3.65	1473	1585	1.93
Cu pic ₂ HgI ₄	1.29	1277	1570	1.92

tetraiodomercurate the magnetic moment for the copper atom was 1.93 ± 0.02 B.M., indicating considerable orbital contribution (Table 3). The salts of the complex were readily decomposed by dilute strong acids, and by boiling with strong alkali reduction to cuprous oxide resulted. Attempts to prepare pure copper(I) complexes directly or by reduction with hydroxylamine, hydrazine, or cyanide were unsuccessful, owing to the formation of cuprous oxide.

II. EXPERIMENTAL

The physical measurements were made in accordance with the methods outlined in previous papers of this series.

(a) *Bis(2-picolyamine) Copper(II) Chloride*.—Cupric chloride (1.35 g; 10mm) in water (10 ml) was treated with 2-picolyamine (2.16 g; 20mm) with shaking. The violet-blue crystalline powder which settled out from the blue solution was separated by centrifuging, washed with ethanol and ether, and dried at 105 °C (yield 3.28 g, m.p. 196 °C) (Found: Cl, 20.2; Cu, 18.0%. Calc. for $C_{12}H_{16}N_4Cl_2Cu$: Cl, 20.2; Cu, 18.2%).

(b) *Bis(2-picolyamine) Copper(II) Bromide*.—Cupric bromide (2.23 g; 10mm) in water (10 ml) was treated with 2-picolyamine (2.16 g; 20mm) and the above procedure repeated. Violet-blue crystals resulted (yield 4.05 g; m.p. 200 °C) (Found: Br, 36.1; Cu, 14.4%. Calc. for $C_{12}H_{16}N_4Br_2Cu$: Br, 36.4; Cu, 14.5%).

(c) *Bis(2-picolyamine) Copper(II) Iodide*.—Cupric chloride (1.35 g; 10mm) in water (10 ml) was treated with a mixture of lithium iodide (2.7 g) and 2-picolyamine (2.16 g; 20mm) in water (10 ml) and the green microcrystalline precipitate which formed treated as in (a) (yield 5.30 g, m.p. 208 °C) (Found: C, 27.1; H, 2.9; I, 47.1; Cu, 12.0%. Calc. for $C_{12}H_{16}N_4I_2Cu$: C, 27.0; H, 3.0; I, 47.5; Cu, 11.9%).

(d) *Bis(2-picolyamine) Copper(II) Nitrate*.—A solution of copper(II) nitrate (1.88 g; 10mm) in water was treated with 2-picolyamine (2.16 g; 10mm) as in (a). Violet-blue cubic crystals were obtained (yield 3.14 g, m.p. 256 °C (decomp.)) (Found: C, 35.4; H, 4.0; Cu, 15.7%. Calc. for $C_{12}H_{16}N_6O_8Cu$: C, 35.7; H, 4.0; Cu, 15.7%).

(e) *Bis(2-picolyamine) Copper(II) Perchlorate*.—Procedure (a) was repeated with the addition of sodium perchlorate (3.0 g) together with picolyamine (2.16 g) in water (10 ml). The purple microcrystalline powder which resulted was found to be almost insoluble in common organic solvents (yield 4.18 g) (Found: C, 30.3; H, 3.4; Cu, 13.2%. Calc. for $C_{12}H_{16}N_4Cl_2O_8Cu$: C, 30.1; H, 3.4; Cu, 13.8%).

(f) *Bis(2-picolyamine) Copper(II) Tetraiodomercurate*.—Copper nitrate (1.88 g; 10mm) in water (20 ml) was treated with 2-picolyamine (2.16 g; 10mm) and a solution of potassium tetraiodomercurate (7.9 g) in water (20 ml) added with stirring. The purple precipitate which formed was treated as in (a) (yield 9.8 g, m.p. 248 °C) (Found: Cu, 6.4; I, 51.0%. Calc. for $C_{12}H_{16}N_4I_4HgCu$: Cu, 6.5; I, 51.4%).

III. ACKNOWLEDGMENT

The author wishes to thank Dr. E. Challen of the Microanalytical Laboratory for carbon and hydrogen analyses.

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ADDITION COMPOUNDS OF TITANIUM

By P. DUNN*

[Manuscript received August 19, 1959]

Summary

The reaction of titanium tetrachloride, chlorotitanium alkoxides, and titanium tetra-alkoxides with ammonia and pyridine has been investigated. Solid, stable, addition complexes are formed; these react further with alcohols to give the fully substituted ester. In some of the ammonia complexes, titanium exhibits covalencies five and six.

I. INTRODUCTION

The reaction between titanium tetrachloride and ammonia has been investigated tensimetrically at low temperatures (Fowles and Pollard 1953). Their observation that titanium tetrachloride octa-ammoniate can be formed only at low temperatures has been confirmed in the present work. It has now been found that the hexa-ammoniate which forms at room temperature (Rosenheim and Schutte 1901) loses ammonia on heating in a vacuum at 120 °C and forms titanium tetrachloride tetra-ammoniate. This compound can be reconverted to the hexa-ammoniate by treatment with dry ammonia gas. Reaction of titanium tetrachloride hexa-ammoniate or tetra-ammoniate with *n*-butanol gives good yields of titanium tetra-*n*-butoxide, while treatment with water liberates all the ammonia as ammonium chloride. Andrew and Nikolskii (1953) have reported a similar reaction between ethanol and titanium tetrachloride octa-ammoniate.

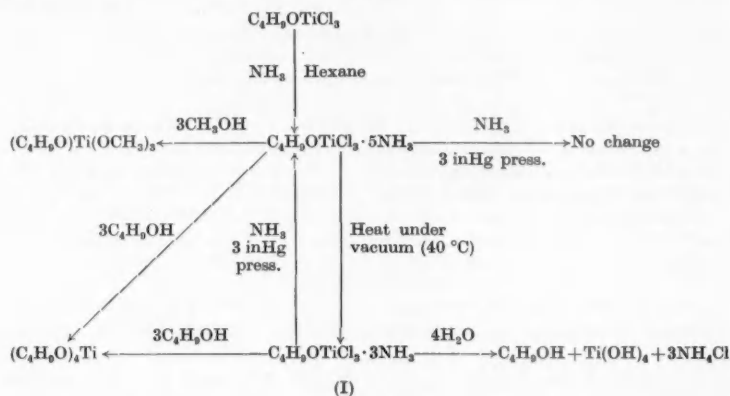
Further, trichlorotitanium mono-*n*-butoxide in hexane solution reacts with gaseous ammonia at room temperature to form trichlorotitanium mono-*n*-butoxide penta-ammoniate. This compound may be converted to trichlorotitanium mono-*n*-butoxide triammoniate either by heating under vacuum or by exposure over phosphorus pentoxide. Both the penta-ammoniate and the triammoniate are insoluble in common organic solvents and react with *n*-butanol to form the tetraorthoester. With methanol the penta-ammoniate forms titanium trimethoxide mono-*n*-butoxide and this reaction has been extended to the preparation of the mixed tetraorthoesters in a one-step process from titanium tetrachloride (Dunn 1959). Water hydrolyses the ammoniates rapidly with the formation of ammonium chloride and butanol.

Similar reactions occur with monochlorotitanium tri-*n*-butoxide, which in hexane solution at 15 °C absorbs 1 mole of ammonia, and on cooling to -5 °C

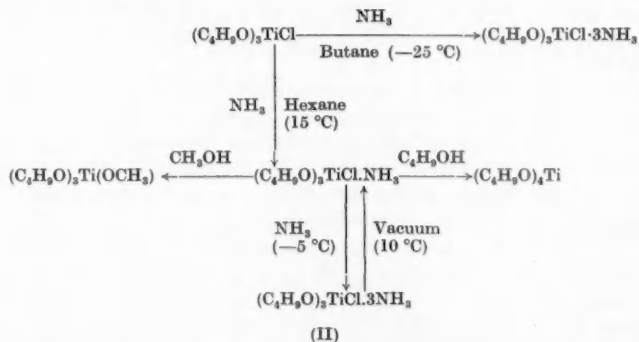
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absorbs a further 2 moles. The triammoniate compound may be readily converted to monochlorotitanium tri-*n*-butoxide monoammoniate by evacuation at 10 °C. The monoammoniate is soluble in hexane.

Since dichlorotitanium di-*n*-butoxide disproportionates readily on fractionation no attempt was made to prepare the ammonia addition compounds of this material.



In boiling hexane, trichlorotitanium mono-*n*-butoxide forms an addition compound with 3 moles of pyridine. Trichlorotitanium mono-*n*-butoxide tripyridinate is soluble in hydrocarbon and chlorinated hydrocarbon solvents and does not react further with pyridine. Reaction with *n*-butanol gives titanium tetra-*n*-butoxide.



Similarly monochlorotitanium tri-*n*-butoxide reacts with 1 mole of pyridine to form the monopyridinate. This compound can be crystallized from aliphatic hydrocarbons and does not react further with pyridine. Even at reduced temperatures, no reaction was observed between pyridine and titanium tetra-*n*-butoxide.

II. DISCUSSION

From the series of compounds prepared it can be concluded that 1 mole of ammonia is added for each mole of chlorine in the compound. Either 1, or more often, 2 moles of ammonia may also be added per mole of titanium. These are no doubt held by coordination valencies to the titanium atom. The thermal stability of the bond increases as replacement of alkoxy groups by chlorine increases.

Fowles and Pollard (1953) have examined the reaction between titanium tetrachloride and liquid ammonia at low temperatures. They concluded that an amido chloride, $Ti(NH_2)_3Cl$, and ammonium chloride are formed. In the present series of reactions of titanium tetrachloride, chlorotitanium alkoxides, and titanium tetra-alkoxides with gaseous ammonia, no ammonium chloride could be detected. The monoammoniate compound formed from monochlorotitanium tri-*n*-butoxide and gaseous ammonia is soluble in hydrocarbon solvents. The greater stability of the bond linking the ammonia and the chlorine, in contrast to the coordination bond linking the ammonia and the titanium, is evidenced by the loss of the ammonia attached to the titanium on heating.

While silicon tetrachloride can form a tetrapyridinate (Trost 1951) and titanium tetrachloride can form a dipyridinate (Piper and Rochow 1954), no evidence of tetrapyridinate formation with titanium tetrachloride was found.

Ammonia will displace pyridine from the pyridinates of titanium tetrachloride and chlorotitanium alkoxides to form the corresponding ammoniates. Thus trichlorotitanium mono-*n*-butoxide tripyridinate can be readily converted to trichlorotitanium mono-*n*-butoxide penta-ammoniate by treatment with gaseous ammonia. With trichlorotitanium mono-*n*-butoxide triammoniate and with titanium tetrachloride tetra-ammoniate it was not possible to displace the ammonia with pyridine.

III. EXPERIMENTAL

Chlorine was determined volumetrically after samples were hydrolysed with methanolic potash. Hydrolysis of samples with concentrated ammonia, followed by ashing, gave the titanium dioxide content. Ammonia was distilled from a sample into saturated boric acid (from a Kjeldahl apparatus) and determined volumetrically. Reactions were carried out with the careful exclusion of moisture.

(a) Ammonia Addition Compounds

(i) *Titanium Tetrachloride Hexa-ammoniate and Titanium Tetrachloride Tetra-ammoniate.*—These compounds were prepared by Rosenheim and Schutte's (1901) method from titanium tetrachloride and dry gaseous ammonia.

Finely powdered titanium tetrachloride tetra-ammoniate was treated with dry gaseous ammonia at a pressure of 3 in Hg above atmospheric for 4 hr at room temperature, the vessel being shaken continuously. Free ammonia was then removed under reduced pressure to give titanium tetrachloride hexa-ammoniate (Found: Cl, 48.5; TiO_2 , 27.2; NH_3 , 34.3%; mol. ratio Cl : TiO_2 , 4.02; mol. ratio NH_3 : Cl, 1.48. Calc. for $C_{18}Cl_4N_6Ti$: Cl, 48.5; TiO_2 , 27.3; NH_3 , 35.0%).

(ii) *Trichlorotitanium Mono-*n*-butoxide Penta-ammoniate.*—Anhydrous ammonia gas was bubbled through a hexane solution of trichlorotitanium mono-*n*-butoxide, m.p. 70–72 °C, b.p. 93 °C/3 mm, at 15 °C for 3 hr. After removal of the solvent by vacuum evaporation, the product

was obtained in a yield of 95% (Found: Cl, 33.9; TiO_2 , 25.6; NH_3 , 26.4%; mol. ratio Cl: TiO_2 , 3.0; mol. ratio NH_3 : Cl, 1.62. Calc. for $\text{C}_6\text{H}_{24}\text{Cl}_3\text{ON}_3\text{Ti}$: Cl, 34.0; TiO_2 , 25.6; NH_3 , 27.2%).

The triammoniate of trichlorotitanium mono-*n*-butoxide was treated with ammonia gas for 4 hr at a pressure of 3 inHg above atmospheric, the reaction vessel being shaken continuously. Free ammonia was then removed under reduced pressure (Found: Cl, 33.6; TiO_2 , 25.2; NH_3 , 27.0%; mol. ratio Cl: TiO_2 , 3.01; mol. ratio NH_3 : Cl, 1.66).

(iii) *Trichlorotitanium Mono-n-butoxide Triammoniate*.—The penta-ammoniate was heated at 40°C for 12 hr under vacuum (1–5 mmHg press.) (Found: Cl, 37.8; TiO_2 , 28.2; NH_3 , 18.8%; mol. ratio Cl: TiO_2 , 3.01; mol. ratio NH_3 : Cl, 1.04. Calc. for $\text{C}_4\text{H}_{12}\text{Cl}_3\text{ON}_5\text{Ti}$: Cl, 38.2; TiO_2 , 28.7; NH_3 , 18.4%).

The triammoniate was also formed by exposure of trichlorotitanium mono-*n*-butoxide penta-ammoniate over phosphorus pentoxide in a vacuum desiccator for 2 days (Found: Cl, 38.2; TiO_2 , 28.1; NH_3 , 17.8%; mol. ratio Cl: TiO_2 , 3.06; mol. ratio NH_3 : Cl, 0.97).

(iv) *Monochlorotitanium Tri-n-butoxide Triammoniate*.—Monochlorotitanium tri-*n*-butoxide, b.p. 164°C/1.0 mm (Cullinane *et al.* 1952) was dissolved in dry butane at –25°C and treated with anhydrous ammonia gas for 3 hr. The solvent was decanted and the crystalline precipitate dried by vacuum evaporation at –30°C (Found: Cl, 9.8; TiO_2 , 22.6; NH_3 , 14.2%; mol. ratio Cl: TiO_2 , 0.98; mol. ratio NH_3 : Cl, 3.00. Calc. for $\text{C}_{12}\text{H}_{36}\text{ClO}_3\text{N}_3\text{Ti}$: Cl, 10.0; TiO_2 , 22.6; NH_3 , 14.4%).

The triammoniate was also formed by treating monochlorotitanium tri-*n*-butoxide mono-ammoniate with dry ammonia gas under a pressure of 3 inHg above atmospheric for 48 hr at a temperature of –5°C (Found: Cl, 9.9; TiO_2 , 22.1; NH_3 , 13.8%; mol. ratio Cl: TiO_2 , 1.01; mol. ratio NH_3 : Cl, 2.91).

(v) *Monochlorotitanium Tri-n-butoxide Monoammoniate*.—Through a solution of monochlorotitanium tri-*n*-butoxide in hexane, at 15°C, dry ammonia was bubbled until the solution was saturated. The solvent and free ammonia were removed under vacuum over a period of 8 hr to give a 96% yield of product. This product was dissolved in dry hexane to give a 10% solution, and insoluble matter removed by centrifuging. After removal of the hexane under reduced pressure and at a temperature not exceeding 20°C, the product was dissolved in dry butane and crystallized at –70°C (Found: Cl, 10.9; TiO_2 , 24.8; NH_3 , 5.0%; mol. ratio Cl: TiO_2 , 0.99; mol. ratio NH_3 : Cl, 0.96. Calc. for $\text{C}_{12}\text{H}_{36}\text{ClO}_2\text{NTi}$: Cl, 11.1; TiO_2 , 25.0; NH_3 , 5.3%).

Evacuation of monochlorotitanium tri-*n*-butoxide triammoniate for 4 hr at 10°C also gave the monoammoniate (Found: Cl, 11.0; TiO_2 , 25.0; NH_3 , 5.4%; mol. ratio Cl: TiO_2 , 0.99; mol. ratio NH_3 : Cl, 1.02).

(vi) *Titanium Tetra-n-butoxide Monoammoniate*.—Ammonia gas was bubbled for 3 hr through a solution of titanium tetra-*n*-butoxide in a light petroleum-ether fraction (b.p. 30–34°C) cooled to –25°C. The solution was then cooled to –50°C when a white solid precipitated. Excess solvent was decanted, and the product obtained in an 82% yield by vacuum evaporation at –50°C. Recrystallization from anhydrous butane at –70°C gave the monoammoniate as fine white needle-like crystals (Found: TiO_2 , 21.6; NH_3 , 4.7%; mol. ratio NH_3 : TiO_2 , 1.02. Calc. for $\text{C}_{16}\text{H}_{40}\text{O}_4\text{NTi}$: TiO_2 , 22.4; NH_3 , 4.9%).

Reaction of liquid ammonia with titanium tetra-*n*-butoxide in butane at –70°C, also gave titanium tetra-*n*-butoxide monoammoniate.

(vii) *Reaction of Ammonia Addition Compounds with Butanol*.—To a stirred suspension of titanium tetrachloride hexa-ammoniate (146 g; 0.5 mole) in dry hexane (800 ml), at 15°C, dry butanol (163 g; 2.2 moles) was added over a period of 1 hr. The white hexane-insoluble ammonium chloride was filtered off and the combined filtrates and washings stripped down under vacuum and distilled. Titanium tetra-*n*-butoxide, b.p. 174°C/3 mm, $n_D^{20}=1.4933$ was obtained in a yield of 70% (Found: TiO_2 , 23.5%. Calc. for $\text{C}_{16}\text{H}_{40}\text{O}_4\text{Ti}$: TiO_2 , 23.5%).

The ammonia addition compounds of monochlorotitanium tri-*n*-butoxide and of trichlorotitanium mono-*n*-butoxide as well as titanium tetrachloride tetra-ammoniate also react with butanol in the manner described above to give titanium tetra-*n*-butoxide.

(b) *Pyridine Addition Compounds*

(i) *Titanium Tetrachloride Dipyridinate*.—This compound was prepared by Piper and Rochow's (1954) method from titanium tetrachloride and pyridine.

(ii) *Trichlorotitanium Mono-n-butoxide Tripyridinate*.—Five m-equiv. of pyridine was added slowly to a hexane solution of trichlorotitanium mono-n-butoxide at 30 °C. The product separated as a viscous liquid which solidified on cooling. After washing with hexane, and drying under reduced pressure, the light coloured free-flowing powder was obtained in a yield of 97% (Found: TiO_2 , 17.8; Cl, 23.3%; mol. ratio Cl:TiO₂, 2.96. Calc. for $\text{C}_{15}\text{H}_{24}\text{Cl}_3\text{N}_3\text{OTi}$: TiO_2 , 17.2; Cl, 22.9%). The tripyridinate was also obtained when 3 instead of 5 moles of pyridine per mole of titanium tetrachloride were used.

(iii) *Monochlorotitanium Tri-n-butoxide Monopyridinate*.—Monochlorotitanium tri-n-butoxide was mixed with 1 m-equiv. of pyridine and the solution then cooled to -25 °C. Butane was added, until the white precipitate just dissolved, and the solution was stored for 2 days at -18 °C. The crystals of monochlorotitanium tri-n-butoxide monopyridinate formed after this time were separated, washed with butane, and dried. On warming to approx. 20 °C the crystals melted to a clear liquid (Found: TiO_2 , 20.6; Cl, 9.5%; mol. ratio Cl:TiO₂, 1.04. Calc. for $\text{C}_{17}\text{H}_{32}\text{ClO}_3\text{NTi}$: TiO_2 , 20.9; Cl, 9.3%).

(iv) *Reaction of Pyridine Addition Compounds with Butanol*.—Titanium tetrachloride dipyridinate (69.6 g; 0.2 mole), or trichlorotitanium mono-n-butoxide (tripyridinate) (93.0 g; 0.2 mole) in boiling hexane (400 ml) was treated dropwise with dry butanol (29.6 g; 0.4 mole) (or excess) over a period of 1 hr. After refluxing for a further 3 hr, the insoluble material was removed by filtration and the filtrate concentrated under vacuum. Fractionation gave titanium tetra-n-butoxide, b.p. 172 °C/3 mm, $n_D^{20} = 1.4398$, in a yield of 35%.

(v) *Exchange Reactions*.—Trichlorotitanium mono-n-butoxide tripyridinate (46.5 g; 0.1 mole) suspended in cooled dry hexane (200 ml) was treated with dry ammonia gas for 8 hr. The yellow, hexane-insoluble, powder was filtered in the absence of air, washed and dried, to give a 97% yield of trichlorotitanium mono-n-butoxide penta-ammoniate. Similarly, titanium tetrachloride dipyridinate was treated with ammonia gas to give a 94% yield of titanium tetrachloride hexa-ammoniate.

IV. ACKNOWLEDGMENT

The present paper is published by permission of the Chief Scientist, Australian Defence Scientific Service, Department of Supply, Melbourne.

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AN INFRA-RED STUDY OF THE ASSOCIATION OF DIAZOAMINO BENZENE

By L. K. DYALL*

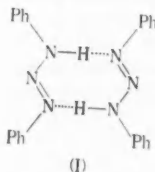
[Manuscript received November 27, 1959]

Summary

The infra-red spectrum of diazoaminobenzene reveals that dimeric association occurs through hydrogen bonding. In tetrachloroethylene solution, the equilibrium constant for dimer formation is found to be $1.2 \pm 0.2 \text{ l mol}^{-1}$. The effects of various solvents on the free N—H stretching frequency have been examined, and the frequency shifts are linearly related to those reported by Bellamy and Hallam (1959) for pyrrole. A linear relation of this type is also found for 2-nitroaniline, and confirms that there is no significant intramolecular hydrogen bonding in this compound.

I. INTRODUCTION

The association of diazoaminobenzene in benzene solution has been reported by Hunter (1937) and by White and Kilpatrick (1955). Cryoscopic measurements revealed a slight degree of cyclic dimeric association. The latter workers determined the equilibrium constant for the association to be $0.52\text{--}0.54 \text{ kg mol}^{-1}$, and the less precise measurements of Hunter confirm this order of magnitude. Hunter, and White and Kilpatrick suggested that the dimeric form has the hydrogen-bonded structure I. This suggestion has been confirmed in the present work, and the effects of various solvents on the infra-red spectrum of diazoaminobenzene have been examined.



II. EXPERIMENTAL

(a) Apparatus

The spectra were recorded as described previously (Dyall and Hambly 1958). Apparent molar extinction coefficients, ϵ_A , were measured directly from recorder charts of the spectrum of the solution and the pure solvent. The spectral slit width at 3300 was 4.7 cm^{-1} . The maximum error in the single ϵ_A values determined in all solvents except tetrachloroethylene would not exceed ± 5 per cent. The values of ϵ_A in the N—H stretching region in tetrachloroethylene solution are the average of two or three determinations, and displayed an average deviation of ± 1 unit. The bandwidth at half maximum absorption, $\Delta\nu_{1/2}$, was also measured directly from recorder traces, and would be expected to show an error of at least $\pm 4 \text{ cm}^{-1}$ since individual frequency measurements in this region were reproducible to $\pm 2 \text{ cm}^{-1}$ (Dyall and Hambly 1958).

(b) Materials

Diazoaminobenzene (B.D.H.) crystallized from light petroleum as golden needles, m.p. 98°C , and was dried *in vacuo* prior to use.

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Tetrachloroethylene, carbon tetrachloride, chloroform, and acetone were purified as described previously (Dyall and Hambly 1958). Ether and benzene were purified by standard methods (Vogel 1951) and were dried over sodium wire. Pyridine (B.D.H.) was dried by refluxing over potassium hydroxide pellets and was then fractionated. *n*-Heptane (May and Baker) and acetonitrile (B.D.H.) were purified by fractionation. Chlorobenzene was purified by shaking, successively, with concentrated sulphuric acid and water, followed by drying (Na_2SO_4) and fractionation.

III. RESULTS

(a) Association of Diazoaminobenzene in Tetrachloroethylene Solution

The results are given in Table 1. The association is of the type $2A \rightleftharpoons A_2$, so that the equilibrium constant K_{eq} is given by $[A_2]/[A]^2$. The proportion of unassociated solute was calculated from a value $\epsilon_A = 93$ for the N—H stretching band at infinite dilution. This value was obtained by extrapolation of a plot of ϵ_A against concentration. The alternative procedure of using a value of ϵ_A

TABLE I
ASSOCIATION OF DIAZOAMINOBENZENE IN TETRACHLOROETHYLENE SOLUTION

Concentration (mol l ⁻¹)	Free N—H Stretching $10^{-3}\epsilon_A$ (cm ² mol ⁻¹)	$\Delta\nu_{\text{NH}}$ (cm ⁻¹)	Bonded N—H Stretching $10^{-3}\epsilon_A$ (cm ² mol ⁻¹)	$\Delta\nu_{\text{NH}}$ (cm ⁻¹)	K_{eq} (l mol ⁻¹)
0.0158	91	15	—	—	—
0.0302	90	16	—	—	—
0.0525	87	18	10	—	—
0.0809	81	16	11	80	1.0
0.1008	73	17	14	81	1.7
0.1514	71	18	19	81	1.3
0.2054	70	17	18	70	1.1
0.2516	69	16	24	64	0.9
0.3122	61	18	28	70	1.3
0.3491	60	19	32	69	1.2
0.3999	57	19	30	82	1.2

obtained at a concentration low enough for there to be no association was not applicable; the overtone band of the N—H deformation and the bonded N—H stretching band overlapped, and it was therefore not possible to determine whether or not the bonded N—H band was absent. Values of K_{eq} were not calculated for concentrations less than 0.08 mol l⁻¹, since values of ϵ_A for more dilute solutions did not differ appreciably by comparison with the experimental error. K_{eq} was found to be 1.2 ± 0.2 l mol⁻¹.

(b) Solvent Effects on the Free N—H Stretching Frequency of Diazoaminobenzene

The values of ν_{NH} in 10 pure solvents are recorded in Tables 2 and 3. These frequencies were also measured in tetrachloroethylene-acetonitrile and tetrachloroethylene-pyridine solutions (Table 3).

(c) *The N—H Deformation Frequency*

The δ_{NH} band appeared either as a shoulder on the strong 1603 cm^{-1} aromatic band or as a broad absorption ($\epsilon_A \sim 40$) whose position was rendered approximate by the overlapping water bands. The frequencies recorded in tetrachloroethylene, chloroform, acetonitrile, and ether were respectively, 1617, 1619, 1613, and 1623 cm^{-1} . The overtone of this band appeared as a weak but distinct shoulder ($3201 \pm 8\text{ cm}^{-1}$) on the bonded N—H stretching band in all solvents except acetonitrile, acetone, pyridine, and ether, in which the overtone band was completely overlapped by the strong, broad, N—H stretching band.

TABLE 2
SOLVENT EFFECTS ON THE FREE N—H STRETCHING FREQUENCY OF DIAZOAMINO BENZENE

Solvent	Concentration Diazamino- benzene (mol l ⁻¹)	Free N—H Stretching Frequency (cm ⁻¹)	$10^{-3}\epsilon_A$ (cm ² mol ⁻¹)	Bonded N—H Stretching Frequency (cm ⁻¹)	$10^{-3}\epsilon_A$ (cm ² mol ⁻¹)
<i>n</i> -Heptane	0.0520	3328	61	—	—
CCl ₄	0.1506	3326	77	3173	27
CHCl ₃	0.1641	3322	73	c. 3190	4
CHCl ₃	0.4060	3320	68	c. 3193	5
PhCl	0.1069	3310	99	c. 3198	10
Benzene	0.0224	3302	83	—	—
Benzene	0.0984	3301	64	3180	12
Benzene	0.2014	3302	70	3179	12
Acetone	0.3023	3227	108	—	—
Ether	0.3110	3205	95	—	—

TABLE 3
N—H STRETCHING FREQUENCIES OF DIAZOAMINO BENZENE IN MIXED SOLVENTS

Main Solvent	Added Solvent	Concen- tration Added Solvent (mol l ⁻¹)	Concen- tration Diazamino- benzene (mol l ⁻¹)	ν_{NH} Free (cm ⁻¹)	$10^{-3}\epsilon_A$ (cm ² mol ⁻¹)	ν_{NH} Bonded (cm ⁻¹)	$10^{-3}\epsilon_A$ (cm ² mol ⁻¹)
C ₂ Cl ₄	—	—	0.2042	3321	59	3176	19
C ₂ Cl ₄	CH ₃ CN	0.155	0.2042	3321	58	3277	17
						3178	17
C ₂ Cl ₄	CH ₃ CN	0.577	0.1828	3322	50	3269	22
						3177	14
C ₂ Cl ₄	CH ₃ CN	3.82	0.1612	3321	35	3265	70
						3184 sh.*	15
CH ₃ CN	—	—	0.3076	—	—	3255	106
C ₂ Cl ₄	—	—	0.3025	3323	61	3181	26
C ₂ Cl ₄	Pyridine	0.195	0.2990	3322	54	3169	36
Pyridine	—	—	0.3046	—	—	3155	82

* sh., shoulder.

(d) Other Bands in the Spectrum of Diazoaminobenzene

The following C—H stretching frequencies, and corresponding apparent extinction coefficients, were recorded in tetrachloroethylene solution in the 3400–1630 cm^{-1} region: 3071(38), 3057(40), 3026(40), 2950(10), and 2866(8); other recorded bands were at 1932(10) and 1918sh.(8). The aromatic ring vibration frequencies at 1603(600), 1595sh.(160), 1587sh.(10), and 1582(5) were identical in tetrachloroethylene, chloroform, acetonitrile, and ether solutions.

TABLE 4
COMPARISON OF SOLVENT EFFECTS ON N—H STRETCHING MODES OF DIAZOAMINO BENZENE, 2-NITRO-ANILINE, AND PYRROLE

Solvent	Diazoaminobenzene		2-Nitroaniline*		Pyrrole† $\Delta\nu/\nu \times 10^3$
	ν_{NH} Free (cm^{-1})	$\Delta\nu/\nu \times 10^3$	$\Delta\nu_{1/2}$ (cm^{-1})	$\Delta\nu/\nu \times 10^3$	
<i>n</i> -Heptane	3328	0	15	0	0‡
CCl_4	3326	0.6	19	—	1.7
CHCl_3	3321	2.1	22	0.9	5.7
PhCl	3310	5.4	28	3.5	7.9
Benzene	3302	7.8	55	4.6	13.7
Nitrobenzene	—	—	—	6.4	16.2
Acetone	3277	15.3	128	11.8	33.1
CH_3CN	3255	21.9	106	—	23.9
Dioxane	—	—	—	16.4	43.6
Ether	3205	36.9	117	—	43.9
Pyridine	3155	52.0	111	—	81.7

* Values of ν_{asym} and ν_{sym} are taken from Dyll and Hambly (1958). The only new measurements are those in *n*-heptane ($\nu_{\text{asym}}=3527$, $\nu_{\text{sym}}=3399 \text{ cm}^{-1}$).

† Bellamy and Hallam (1959).

‡ Bellamy and Hallam used *n*-hexane.

IV. DISCUSSION

(a) Evidence for Association of Diazoaminobenzene

With increasing concentration in tetrachloroethylene solution, the 3322 cm^{-1} band (corresponding to the free N—H stretching motion) decreased in intensity, and an increasingly strong, broad band appeared near 3180 cm^{-1} . This behaviour leaves no doubt that the dimeric association of diazoaminobenzene occurs via hydrogen bonding, and supports the suggestion of Hunter (1937) that the tautomerism of this compound is due to hydrogen exchange within the hydrogen-bonded complex I. The strength of the hydrogen bonds is indicated by observing (Tables 2 and 3) that, of the solvents used in this work, only pyridine formed a stronger bond with the amino group of diazoaminobenzene.

Tetrachloroethylene, since it interacts less strongly than benzene with the amino group of diazoaminobenzene (see Table 4), is expected to favour the formation of the hydrogen-bonded dimer I. In accord with this prediction, $K_{\text{eq}}=0.53 \text{ kg mol}^{-1}$ in benzene solution* (White and Kilpatrick 1955) and

* K_{eq} would be approximately 0.471 mol^{-1} .

$1.2 \pm 0.21 \text{ mol}^{-1}$ in tetrachloroethylene solution. The extent of association in benzene solution was not great enough to permit an infra-red spectroscopic determination of the equilibrium constant (see Table 2).

(b) *Solvent Effects*

Solvent effects on X—H stretching frequencies have been studied recently by Bellamy, Hallam, and Williams (1958), Bellamy (1959), and Bellamy and Hallam (1959), who usually found a smooth progression in the extent of hydrogen bonding with different solvents. This smooth progression can be shown by plotting the relative frequency depression, $\Delta\nu/\nu$ (where ν is the frequency in a paraffinic standard solvent such as *n*-hexane) for the compound under study, against $\Delta\nu/\nu$ for the N—H stretching frequency of pyrrole. With diazoamino-

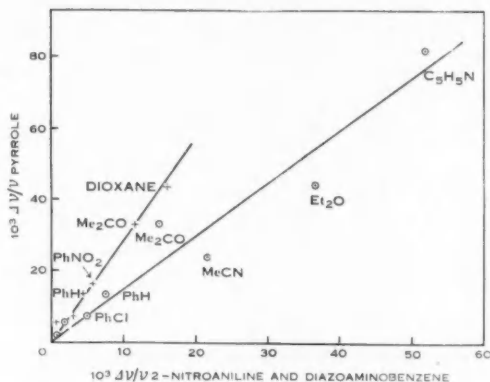


Fig. 1.—Solvent effects on N—H stretching frequencies.

benzene, the value of ν_{NH} might be expected to be affected, not only by hydrogen bonding to the solvent, but also by solvent effects on the adjacent azo group. The plot is nevertheless linear (see Table 4 and Fig. 1) and the only marked deviation from the behaviour of pyrrole is the inverted positions of acetone and acetonitrile on the plot. The progressive lowering of ν_{NH} in Table 4, is, as reported by Bellamy, Hallam, and Williams (1958), accompanied by broadening of the N—H stretching band.

A far more rigorous test of Bellamy's theory of solvent effects is the case of 2-nitroaniline. The N—H stretching frequency is markedly dependent upon the electrical effect of the nitro group (Dyall and Hamblly 1958). The highly polar nitro group should be subject to strong solvent effects, and the observed changes in N—H stretching frequencies should thus be the resultant of the separate solvent effects on the amino and nitro groups. Surprisingly, the solvent effects on the (average) N—H stretching frequency, when plotted against the same effects for pyrrole, yield a linear plot (see Table 4 and Fig. 1). The deviations are actually no larger than those reported by Bellamy, Hallam, and Williams (1958) for aniline. The linearity of the plot for 2-nitroaniline supports our

conclusion (Dyall and Hambly 1958) that there is no significant intramolecular hydrogen bonding in 2-nitroaniline. When strong intramolecular hydrogen bonds are present (as in 8-hydroxyquinoline and 2-nitrophenol), Bellamy and Hallam (1959) report a sharp break in the plot when the solvent is able to form an intermolecular hydrogen bond stronger than the intramolecular bond.

The slopes of the linear plots indicate (Bellamy, Hallam, and Williams 1958) that the order of decreasing acidity of the amino hydrogens is diazoaminobenzene > 2-nitroaniline > aniline.

The results in Table 3 substantiate the work of Bellamy and Hallam (1959) with mixed solvents. Diazoaminobenzene shows three N—H stretching bands (two solvent-bonded and one intermolecularly self-bonded) in tetrachloroethylene-acetonitrile and tetrachloroethylene-pyridine mixtures. The intensities of the two bands due to solvent-bonded N—H vibrations are dependent on the relative concentrations of the two solvents.

V. ACKNOWLEDGMENTS

The author thanks Professor A. N. Hambly of Canberra University College for his interest in this work, and Monsanto Chemicals (Australia) for a research scholarship.

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THE INTERACTION BETWEEN COPPER AND SODIUM DODECYL SULPHATE SOLUTIONS IN THE PRESENCE OF AIR

By B. D. CUMING* and J. H. SCHULMAN†

[Manuscript received July 20, 1959]

Summary

The interaction of oxide-covered copper powder with solutions of sodium dodecyl sulphate has been studied as a function of pH. In acid solutions copper ions dissolve from the oxide layer, the pH rises, and dodecyl sulphate is precipitated, probably as the basic cupric salt. If the final pH is greater than about 4, adsorption of dodecyl sulphate also occurs. There is a range of pH (6-8.5 under the conditions used) where precipitation is negligible or does not occur, but where adsorption is strong. Above this range, adsorption becomes weaker, and at high pH there is little or no reaction. The pH limits for these phenomena will vary with the dodecyl sulphate concentrations and with other conditions. The results are analysed in terms of the interfacial and solution equilibria in the system.

I. INTRODUCTION

An earlier paper (Cuming and Schulman 1953) reported a study of the uptake of dodecyl sulphate by copper from solutions at pH 6. The work now described deals with the interaction of dodecyl sulphate with copper as a function of pH. The results illustrate the competitive relationship existing between adsorption and corrosion reactions when surface active anions interact with the oxide film on a metal. This relationship will be considered in terms of the chemical equilibria at the solid surface and in solution.

The previous work showed that two layers of dodecyl sulphate are adsorbed at saturation, the first being chemisorbed and the second amphipathically adsorbed with the reverse orientation. To avoid the complication of second layer adsorption in the present experiments, a concentration of $1.5 \times 10^{-3}M$ was chosen, corresponding to a point near the middle of the monolayer plateau in the concentration isotherm for pH 6. The removal of dodecyl sulphate could therefore be attributed only to chemisorption or precipitation.

The monolayer capacity of the powder was measured by the B.E.T. method, using krypton at $-195^{\circ}C$, and by the adsorption of stearic acid from light petroleum solution.

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II. EXPERIMENTAL

(a) Copper Powder

"Air-atomized" copper of -300 mesh particle size (supplied by the Powder Metallurgy Co. Ltd.) was used. The particles were spherical, and had a bright, smooth appearance under the microscope, indicating that the natural oxide layer must have been thin and uniform. Preliminary experiments showed that washing with organic solvents had no effect on the adsorption behaviour, and the powder was used as received.

(b) Methods

The methods used in the adsorption of stearic acid and krypton, and in the estimation of dodecyl sulphate, have been described previously (Cumming and Schulman 1959). A Cambridge pH meter with a glass electrode was used for pH measurements.

(c) Procedure

A stock solution of sodium dodecyl sulphate was diluted for each measurement to $1.5 \times 10^{-3}M$, and a calculated volume of H_2SO_4 or NaOH solution added at the same time to adjust the pH to the value required. Acid solutions were unbuffered, but those on the alkaline side were buffered with $M/1000$ borate or $M/100$ bicarbonate; a few experiments with unbuffered alkaline solutions gave similar results, but the drift due to CO_2 absorption was too great. A 5 ml aliquot of the diluted solution was used in each measurement, and the remainder was used to determine the initial pH and to check the concentration of dodecyl sulphate. This concentration was found not to decrease, within experimental error, in the time taken for the experiment, indicating that there was no appreciable hydrolysis of dodecyl sulphate even at the lowest pH values. The 5 ml aliquot was shaken with a weighed sample of copper for 30 min and the supernatant solution was then decanted and centrifuged; 1 ml was removed for dodecyl sulphate estimation and the remainder was used to determine the final pH. The accuracy of the uptake results was about ± 4 per cent. Small errors may be present in the pH values for the unbuffered systems due to exposure to the atmosphere.

III. RESULTS

The monolayer capacity of the powder for krypton was found to be 4.3×10^{-7} mole g^{-1} . The stearic acid method gave a lower value, 2.6×10^{-7} mole g^{-1} . Experience with a number of different samples has shown that it is difficult to obtain closely reproducible results with the stearic acid method (Cumming and Schulman, unpublished data), whereas krypton adsorption is readily reproducible. The value of 4.3×10^{-7} mole g^{-1} is therefore more reliable, although it probably yields too high a value for the dodecyl sulphate capacity (Cumming and Schulman 1953). The true capacity probably lies between 3×10^{-7} and 4×10^{-7} mole g^{-1} .

Typical interaction results are given in Figure 1, in which the amount of DS^- ion removed from solution by interaction with the copper powder is plotted against both the initial pH and the final pH. In this series of measurements,

3 g of copper was reacted with 5 ml of solution. In other series where the w/v ratio was different, the behaviour was similar but the gradient of the initial pH curve varied in the low pH region. For all w/v ratios the flat part of the uptake *v.* final pH curve lay between approximately the same limits.

A number of precipitation and flotation tests has also been carried out, the results of which are interpolated at appropriate points in Section IV.

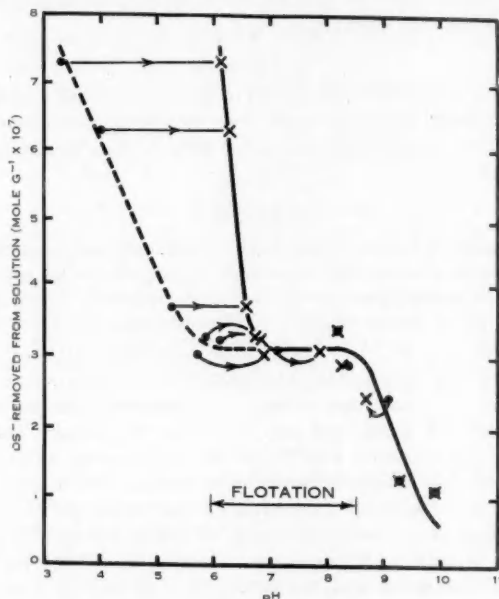


Fig. 1.—Amount of dodecyl sulphate removed from solution by copper powder after 30 min. Plotted against initial pH (●) and final pH (×). An arrow connects points for the same experiment. 3 g Cu in 5 ml $1.5 \times 10^{-3}M$ dodecyl sulphate.

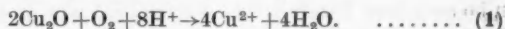
IV. DISCUSSION

It will be seen from Figure 1 that there are three pH regions in which the interaction behaviour is substantially different. Each of these will be discussed in turn.

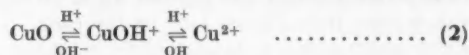
(a) Corrosion Region ($pH < 6$)

When the copper powder was added to acidified solutions of sodium dodecyl sulphate, the pH rose to values of about 6 or 7, as indicated by the arrows in Figure 1. The uptake of dodecyl sulphate was high and a precipitate was visible in the solution. Evidently copper was dissolved from the surface and precipitated from solution by the dodecyl sulphate. In addition, it was observed that the powder became hydrophobic, indicating that dodecyl sulphate was adsorbed. The DS⁻ uptake measured was the sum of the amounts precipitated and adsorbed.

The air-formed oxide film on the surface of the copper particles was probably Cu_2O (Evans 1946). At low pH, and in the presence of oxygen, the oxide dissolves and the pH increases according to the equation



The dissolved oxygen likewise oxidizes the surface layers of the residual oxide to CuO (Pourbaix 1949). Corrosion will therefore continue until the system



is in equilibrium. The conditions for this are given by equation (3) (Pourbaix 1949) and equation (4) (Pedersen 1943), and are represented graphically by *ABC* and *DEF* in Figure 2.

$$\log_{10} [\text{Cu}^{2+}] = 7.6 - 2 \text{ pH} \quad (3)$$

$$\log_{10} \frac{[\text{CuOH}^+]}{[\text{Cu}^{2+}]} = -8 + \text{pH} \quad (4)$$

From equations (1) and (3) the amount of copper dissolved and the final pH which would be reached in the absence of dodecyl sulphate can be calculated

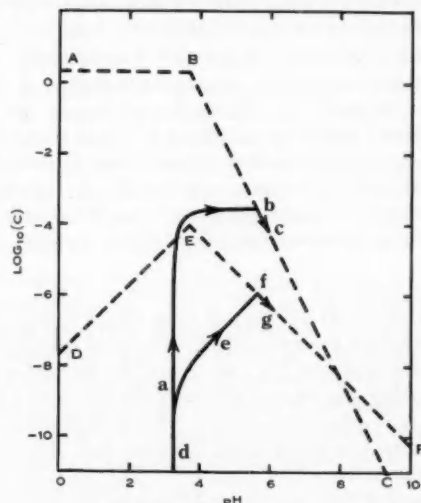


Fig. 2.—Calculated concentration-pH relations for Cu^{2+} ion (*ABC*) and CuOH^+ ion (*DEF*) in equilibrium with CuO . See text for explanation of curves *abc* and *defg*.

for a given initial pH. For example, if the initial pH were 3.25, there would be sufficient hydrogen ions available to liberate $2.8 \times 10^{-4} \text{ M}$ copper ions into solution, and the equilibrium pH (from eqn. (3)) would be 5.6; the course of this reaction is plotted as *ab* in Figure 2. When dodecyl sulphate is present, however, it reacts with the dissolved copper to form a precipitate. This causes a

further shift in the equilibrium represented by equation (2) (*bc* in Fig. 2) and the final pH will be higher; its value will depend on the concentration of dodecyl sulphate and the solubility product of the precipitate. For the example taken, it can be seen from Figure 1 that the final pH was, in fact, 6.1.

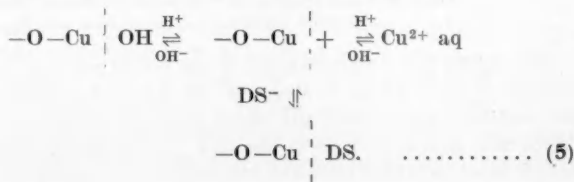
If the initial pH is higher, fewer H^+ ions are available and so a smaller amount of copper is dissolved. The amount of DS^- ion removed from solution by precipitation may therefore be expected to decrease with increasing initial pH and this is seen from Figure 1 to be the case.

Experiments with solutions of copper sulphate and sodium dodecyl sulphate have indicated that the precipitate formed is not the simple salt $Cu(DS)_2$, but a basic salt. For example, in a solution containing 10^{-3} mole l^{-1} DS^- ion and 10^{-2} mole l^{-1} Cu^{2+} ion, no precipitation was observed until the pH was raised to 4.2. Similar results were obtained for Cu^{2+} concentrations of 10^{-3} and 10^{-4} mole l^{-1} , the pH values for precipitation being 5.4 and 6.2 respectively. These results are only approximate since the exact onset of precipitation is difficult to observe, but they show clearly that the insoluble dodecyl sulphate compound is formed only at a pH where the $CuOH^+$ concentration is comparatively high, indicating that it must be a basic salt. This was supported by the fact that the product $[CuOH^+][DS^-]$ was constant within the experimental limits, the values being 2.0×10^{-9} , 2.5×10^{-9} , and 1.6×10^{-9} mole² l^{-2} for Cu^{2+} concentrations of 10^{-2} , 10^{-3} , and 10^{-4} mole l^{-1} respectively.

The overall reaction between the copper oxide surface and dodecyl sulphate in solution, therefore, involves the dissolution of copper, during which $[Cu^{2+}]$ rises according to a curve such as *ab* in Figure 2, whilst $[CuOH^+]$ follows a curve such as *def*. At the point *f* (or just before it), the solubility product $[CuOH^+][DS^-]$ is exceeded and precipitation occurs. As $CuOH^+$ is removed from solution, copper oxide continues to dissolve—so that the pH continues to rise—until equilibrium is established between CuO , $Cu(OH)DS$, and the ions in solution.

(b) *Region of Strong Adsorption (pH 6-8.5)*

In the solutions of initial pH greater than about 6, the amounts of copper which could be dissolved by the available H^+ ions were calculated to be negligible compared with the amounts of DS^- ion found to be removed from solution. It is clear, therefore, that the plateau region of the curve at a level of 3.0×10^{-7} mole g^{-1} must represent adsorption only. This is supported by the values of the monolayer capacity calculated from krypton and stearic acid adsorption, which indicate a value of 3.4×10^{-7} mole g^{-1} . The adsorption can be regarded simply as the exchange of DS^- ions for OH^- ions on the hydrated surface of the oxide, and the surface equilibria can be described as follows:



It is clear that increasing H^+ ion concentration favours positive ionization of the surface, and therefore favours the adsorption of dodecyl sulphate.

The surface compound formed may be likened to basic copper dodecyl sulphate—the compound which appears to be precipitated during corrosion—and it is not surprising that the surface and bulk compounds are stable in about the same pH range. In fact, however, strong adsorption persists up to about pH 8.5, whereas the approximate value obtained for the solubility product of $Cu(OH)DS$ indicates that bulk precipitation could not have occurred above pH 6. This suggests that the surface compound is rather more stable than the three-dimensional compound; such behaviour is in conformity with many other observations of the enhancement of stability by adsorption.

The results plotted in Figure 1 do not tell us whether or not adsorption occurs below pH 6, since it is impossible to separate the adsorption and precipitation components of the total uptake of dodecyl sulphate. Flotation observations throw some light on this problem. In the course of the uptake experiments it was noted that flotation was excellent at pH values from 8.5 down to 5.5, provided the w/v ratio and the initial pH were such that an oxide layer remained after corrosion. If, however, the oxide was completely dissolved, flotation was poor or absent. Separate flotation experiments have been carried out in which the copper powder was washed under nitrogen with an excess of acid and then with deoxygenated water to reveal and maintain the bare metallic surface; the pH was adjusted to various values between 4 and 6, and sodium dodecyl sulphate added at a concentration of $10^{-3}M$. There was no flotation, confirming the fact that dodecyl sulphate is not adsorbed on copper metal, but only on the oxide. In support of this it was found that the admission of air slowly restored flotation. Since CuO is unstable when the pH is less than 3.8 (see Fig. 2) adsorption certainly cannot occur below this value.

In addition, there is a limit to the adsorption range set by the stability of basic cupric dodecyl sulphate. Using the solubility product derived above, it can be calculated that the concentration of DS^- ion which can exist in equilibrium with both CuO and $Cu(OH)DS$ is reduced to about 10^{-4} mole l^{-1} at pH 4. The precipitation reaction therefore competes strongly for dodecyl sulphate, and adsorption would be expected to diminish as the pH falls from 5.5 to 4. Experimentally it was not found possible to achieve final pH values in this region with the powder used, without dissolving off the oxide layer. This point is therefore unchecked.

(c) Region of Weak Adsorption (pH > 8.5)

As the pH is increased, the OH^- ion competes more successfully with the DS^- ion (see eqn. (5)), and adsorption decreases. The decrease is seen from Figure 1 to start at about pH 8.5. This pH value is a function of the final concentration of DS^- in solution. Thus we would expect that at a higher DS^- ion concentration a higher OH^- ion concentration would be required for displacement of DS^- from the surface. Increasing $[DS^-]$ should therefore displace the curve to the right and decreasing $[DS^-]$ should displace it to the left.

(d) Effect of [DS⁻] on the Whole Curve

It is interesting to notice that a tenfold decrease in [DS⁻] should also decrease the pH to which precipitation persists by one unit. Thus, from the relation

$$[\text{CuOH}^+][\text{DS}^-] = K_s,$$

and equations (3) and (4), it follows that the maximum pH for precipitation is given by

$$\text{pH}_{\text{pptn}} = \log_{10} [\text{DS}^-] - \log_{10} (K_s) - 1.4.$$

This has been confirmed experimentally in precipitation experiments with CuSO₄ solutions.

The uptake curve will therefore retain approximately the same form and simply move as a whole along the pH axis when the dodecyl sulphate concentration is changed. It is important to realize, however, that this behaviour is limited at the lower end of the [DS⁻] scale by the instability of CuO below pH 4, and at the upper end of the scale by the onset of two-layer adsorption (Cuming and Schulman 1953) which will result in more complicated relations between adsorption and precipitation as functions of pH and [DS⁻]. Furthermore, above the micelle point [DS⁻] remains practically constant, and this sets a limit to the maximum pH for first-layer adsorption, quite apart from the complication of second-layer adsorption.

V. CONCLUSIONS

Section IV has suggested a close relationship between the adsorption of long-chain anions on an oxide surface and the precipitation in bulk of the corresponding basic salt. It follows that the behaviour in any such system should be semiquantitatively predictable if we knew the constants describing the ionic equilibria for the oxide/metal ion system together with the solubility product of the basic salt formed with the adsorbate. Failing this information, Langmuir trough experiments in which metal ions are injected under insoluble films of a substance similar to the adsorbate can be a guide (see e.g. Wolstenholme and Schulman 1950; Thomas and Schulman 1954*a*, 1954*b*; Spink and Sanders 1955). The correlation between adsorption and the behaviour of the insoluble films is fairly complex. It can be shown that exact correspondence between pH ranges of maximum adsorption and film solidification would not be expected, but the displacement of these ranges for different metals should be parallel. Thomas and Schulman found maximum interaction at pH 6 for hexadecyl sulphate on M/2000 CuSO₄; this behaviour has been shown to be in satisfactory agreement with the present adsorption results.

At the concentration of dodecyl sulphate used in these experiments, an initial pH of 6 leads to strong adsorption accompanied by a negligible amount of precipitation. If the concentration were increased to 10⁻²M, the predicted displacement of the adsorption-pH curve (Section IV (d)) suggests that some precipitation may occur at pH 6, but it would probably not exceed 10 per cent. of the adsorption. We can conclude, therefore, that the uptake isotherm reported

previously (Cuming and Schulman 1953) mainly represents adsorption, so that it provides valid evidence for the adsorption of a second layer of dodecyl sulphate ions.

VI. ACKNOWLEDGMENTS

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REACTIONS OF ALKOXY RADICALS

I. THE REACTIONS OF DI-*tert*.-BUTYL PEROXIDE WITH *n*-BUTYRIC ACID AND ETHYL *n*-BUTYRATE

By A. L. J. BECKWITH*

[Manuscript received October 21, 1959]

Summary

The relative yields of *meso*- and *racemic*-2,3-diethylsuccinic and 2-ethyl-3-methylglutaric acids from the reaction of di-*tert*.-butyl peroxide with *n*-butyric acid indicate that abstraction of hydrogen atoms from the acid by *tert*.-butoxy radicals occurs preferentially at the α -position. A similar directive effect has been noted in the reaction of ethyl *n*-butyrate with di-*tert*.-butyl peroxide. These results suggest that the *tert*.-butoxy radical has negligible electron-acceptor properties and that polar effects do not influence the course of its reactions. Catalytic amounts of cupric chloride profoundly modify the reaction of di-*tert*.-butyl peroxide with *n*-butyric acid.

New analytical methods for the separation and determination of hydroxy- and dicarboxylic acids are described.

I. INTRODUCTION

Alkyl and aryl radicals react with saturated acids by abstraction of hydrogen atoms from the α -position. The 1-carboxyalkyl radicals so produced may undergo further reactions such as dimerization, disproportionation, or coupling with other free radicals. Thus free methyl radicals, generated by thermal decomposition of acetyl peroxide, convert acetic acid to succinic acid, *isobutyric* acid to 2,2,3,3-tetramethylsuccinic acid, and haloacetic acids to the appropriately substituted succinic acids (Kharasch and Gladstone 1943; Kharasch, Jensen, and Urry 1945). 2,3-Dimethylsuccinic acid and 2-phenylpropionic acid are produced by heating benzoyl peroxide in propionic acid (Goldschmidt 1957). The activation of the α -position in acids towards hydrogen abstraction by alkyl radicals appears to be a function of the carbonyl group, since the same directive influence has been observed in similar free-radical reactions of acid chlorides (Kharasch, Jensen, and Urry 1945; Price and Morita 1953), esters (Kharasch, McBay, and Urry 1945), and ketones (Kharasch, McBay, and Urry 1948; Ansell, Hickinbottom, and Holton 1955).

On the other hand, the carbonyl group evidently deactivates the α -position towards attack by halogen atoms for photochlorination of aliphatic acids, acid chlorides, and esters occurs preferentially at positions remote from the carbonyl group (Bruylants, Tits, and Dauby 1949; Bruylants *et al.* 1952). It has been suggested that the β -position has enhanced reactivity but this is not supported by a recent investigation of the chlorination of fatty acid chlorides (Smit and Hertog 1958).

Directive effects in hydrogen-abstraction reactions have been discussed by Walling (1957, p. 365) and Russell (1958, 1959), who have suggested that polar

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effects influence the course of such reactions. Thus, for attack by weakly nucleophilic alkyl radicals C—H bond strength is the determining factor and the reaction with acids proceeds through abstraction of hydrogen from the α -position to the radical stabilized by resonance with the carbonyl group. However, the electron-attracting character of the C=O group deactivates adjacent positions in carbonyl compounds towards attack by strongly electrophilic halogen atoms.

On this basis one might predict that alkoxy radicals, which Walling (1957, p. 470) regards as being weakly electrophilic, should suffer the same directive influences as halogen atoms but at present there is little experimental data to support this supposition. Gray and Williams (1959) have stated that the α -position in ketones is activated towards attack by alkoxy radicals and this has been observed by Moore (1951) for the reactions of *tert.*-butoxy radicals with butan-2-one and cyclohexanone.

Reactions of other oxygen-containing radicals with carbonyl compounds have been studied. Autoxidation, which involves abstraction of hydrogen by alkylperoxy radicals, occurs at the α -positions in 4-heptanone (Sharp *et al.* 1952), but with esters, which react only slowly at elevated temperatures, the reaction proceeds at points remote from the carbonyl group (Rigg and Gisser 1953).

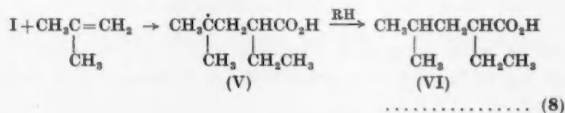
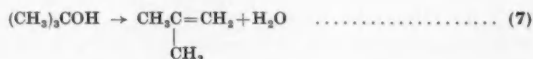
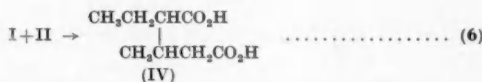
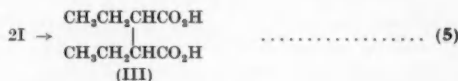
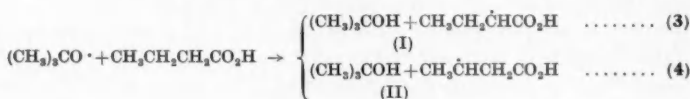
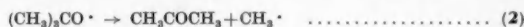
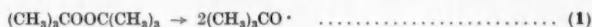
The hydroxyl radicals produced by Fenton's method appear to be particularly reactive and attack all available carbon-hydrogen bonds. A recent investigation (Coffman, Jenner, and Lipscomb 1958) has shown that carbonyl compounds are dimerized by Fenton's reagent, and usually all possible dimers are formed. However, the course of the reaction with propionic, butyric, and isobutyric acids has given rise to the suggestion that "hydroxyl radicals and chlorine atoms have qualitatively similar preferences in attack on carbon-hydrogen bonds". Perusal of the experimental section reveals that this conclusion is hardly justified. From the reaction with butyric acid six products were detected by examination of the refractive indices of the fractions from distillation but only three of these were isolated (unspecified yield) and identified by comparison of melting points with literature values. This method is obviously unsatisfactory for among the nine dibasic acids obtainable by dimerization of butyric acid there are several examples of pairs with very similar melting points. Thus the acid identified as *meso*-3,4-dimethyladipic acid, m.p. 133 °C (Faltis and Wagner 1923), might well be *racemic*-2,3-diethylsuccinic acid, m.p. 132–133 °C (Ebersen 1959), while the acid m.p. 104 °C could be either *racemic*-3,4-dimethyladipic acid, m.p. 104–105 °C, 115.5–116.5 °C (Faltis and Wagner 1923; Stallberg-Stenhagen 1951), or the high-melting isomer of 2-ethyl-3-methylglutaric acid, m.p. 101–102 °C (Mumm *et al.* 1937).

The dimerization of aliphatic acids in flames (Cleaver, Blosser, and Coffman 1959) or by ultraviolet irradiation (Pfordte and Leuschner 1959) undoubtedly proceeds by a free-radical mechanism, but there is as yet no evidence as to whether these reactions involve hydrogen abstraction by oxygen-containing radicals. Similarly, the dimerization of propionic acid by electrolysis or by treatment with propionyl peroxide (Goldschmidt 1957) may occur through attack by either ethyl or propionyloxy radicals.

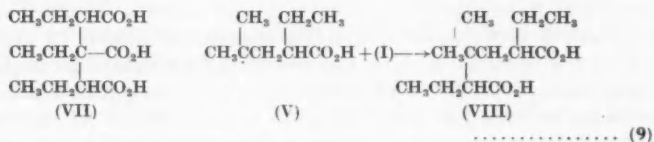
The present work, which is part of a general study of oxidation mechanisms in aliphatic compounds, was designed to determine more precisely the directive influence of the carboxyl group on the course of reactions involving free-alkoxy radicals. The radical source employed was di-*tert*.-butyl peroxide which undergoes thermal decomposition to *tert*.-butoxy radicals under a wide range of conditions and has been shown to be a highly effective reagent for hydrogen-abstraction reactions (Raley, Rust, and Vaughan 1948; Brooks 1957; Williams Overright, and Brooks 1957). Since the further decomposition of *tert*.-butoxy radicals to methyl radicals is favoured by increase in temperature these reactions were conducted at the lowest convenient temperature (116 °C).

II. DISCUSSION

The yields of products obtained from the decomposition of 10 g of di-*tert*.-butyl peroxide in butyric acid were as follows: acetone, 1.9 g (24%); *tert*.-butanol, 6.1 g (60%); *meso*-2,3-diethylsuccinic acid, 2.6 g (22%); *racemic*-2,3-diethylsuccinic acid, 2.4 g (20%); 2-ethyl-3-methylglutaric acid, 0.32 g (2.6%); *tert*.-butyl butyrate, (0.65 g); and 2-ethyl-4-methylvaleric acid, (0.34 g). The yields of acetone and *tert*.-butanol provide a measure of the relative rates of reactions (1) and (2), and indicate that abstraction of hydrogen from the substrate was substantially carried out by *tert*.-butoxy radicals. The isomeric 2,3-diethylsuccinic acid (III) and 2-ethyl-3-methylglutaric acid (IV) obviously arise by coupling of the radicals formed in reactions (3) and (4). The *tert*.-butanol formed in (3) and (4) leads by further reactions to two minor products; *tert*.-butyl butyrate results from direct esterification during the lengthy reaction period, while 2-ethyl-4-methylvaleric acid (VI) must be formed by radical addition to isobutylene according to equations (7) and (8).

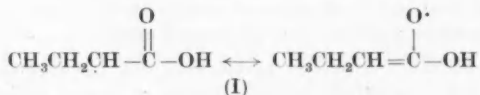


Amongst the unidentified products was a water-soluble acid which was isolated only after prolonged extraction with ether of the aqueous solution. This may well be the tricarboxylic acid (VII) which would be expected to result from further free-radical reactions of 2,3-diethylsuccinic acid. The similar formation of trichlorotricarballylic ester by treatment of methyl chloroacetate with acetyl peroxide has been previously reported (Kharasch, Jensen, and Urry 1945).



One would anticipate that the radical V, which is an intermediate in the formation of 2-ethyl-4-methylvaleric acid (VI), would also lead to the dicarboxylic acid (VIII) by reaction with a further radical I according to equation (9). The expected product was not obtained pure but may be present in an oily fraction whose equivalent weight and chromatographic behaviour were consistent with its formulation as a C_{12} dibasic acid. Another unidentified product was an acid, $\text{C}_8\text{H}_{12}\text{O}_4$, which was isolated in very small yield as the phenylphenacyl ester. The presence of a strong absorption band in the infra-red at 1786 cm^{-1} may be indicative of a γ -lactone grouping but otherwise nothing is known of the structure. Possibly some of the unidentified substances in the reaction mixture arise by attack of free radicals on the acetone formed by reaction (2).

The yields of 2,3-diethylsuccinic and 2-ethyl-3-methylglutaric acids are proportional to the concentrations in the reaction mixture of radicals I and II and hence provide a measure of the relative rates of reactions (3) and (4). It is apparent that *tert*-butoxy radicals react at the α -position of butyric acid approximately 16 times more rapidly than at the β -position. Evidently the most important factor in determining the course of the reaction is the stability of the radical I which is a resonance hybrid of the following contributing structures:

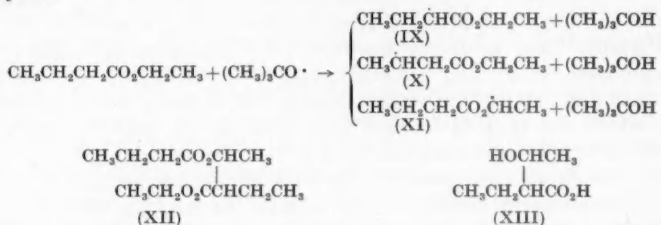


The slow rate of attack at the β -position also indicates that *tert*-butoxy radicals have no pronounced electron-acceptor properties (Walling 1957, p. 470) for the electron-attracting carbonyl group deactivates the α -position towards attack by electrophilic reagents.

These conclusions would be invalid if the radical obtained by attack of a *tert*-butoxy radical at the β -position of butyric acid selectively abstracted hydrogen from the α -position of another acid molecule. However, preliminary experiments with electrophilic radicals indicate that this reaction sequence, which could mask the true character of the *tert*-butoxy radical, does not occur to any great extent. The attack of *tert*-butoxy radicals on butyrate ions rather

than free-butyric acid molecules could also obscure the true nature of the alkoxy radical, for the carboxylate group is electron-repelling and assists attack of electrophilic reagents at the α -position. To investigate this possibility the decomposition of di-*tert*-butyl peroxide in ethyl *n*-butyrate was studied.

The extent to which the various positions in ethyl butyrate were attacked by *tert*-butoxy radicals was estimated by hydrolysis of the product mixture. Only those compounds arising from coupling reactions of the radical XI are hydrolysed to give butyric acid which is readily separable by steam distillation. Other products were formed by coupling reactions of radicals IX and X as was shown by the isolation of *meso*- and *racemic*-2,3-diethylsuccinic and 2-ethyl-3-methylglutaric acids after hydrolysis. The compound XII which would be expected to be formed by coupling of the radicals IX and XI was not isolated but a small quantity of unsaturated acid which was detected by chromatography on paper probably arose by dehydration of the hydroxy acid (XIII) after hydrolysis.



As with the free acid, attack of *tert*-butoxy radicals on ethyl butyrate was very largely confined to the position α to the carbonyl group. The reaction proceeded approximately six times more readily in the acid moiety than in the alcohol component of the ester. The amounts of *meso*- and *racemic*-2,3-diethylsuccinic and 2-ethyl-3-methylglutaric acids obtained after hydrolysis of the product were in the ratio of 5:5:1 indicating that the α -position in the acid moiety was attacked some 10 times more readily than the β -position.

These results accord with those obtained from the reaction with butyric acid and indicate that polar effects have very little influence on the course of reaction of *tert*-butoxy radicals with acids and esters.

The final experiment described herein concerns the reaction of *n*-butyric acid with di-*tert*-butyl peroxide in the presence of cupric chloride. Catalytic amounts of copper salts have been shown recently to influence markedly the course of free-radical reactions (Kharasch and Fono 1958, 1959; Kharasch and Sosnovsky 1958*a*, 1958*b*), and in particular lead to the replacement of hydrogen by the attacking radical in active hydrogen donors.

The reaction product obtained by decomposition of di-*tert*-butyl peroxide in butyric acid with a small amount of cupric chloride was extremely complex and has not yet been successfully analysed. The most notable feature was the absence of the dimeric acids obtained from the same reaction without copper salts. Small amounts of acids $\text{C}_8\text{H}_{14}\text{O}_4$ and $\text{C}_8\text{H}_{12}\text{O}_4$ were isolated in the form of crystalline derivatives but were not identified, and the presence of unsaturated

compounds and lactones in the product mixture was detected. Until the products have been more fully identified it is not possible to comment on the reaction mechanism except to draw attention to the great differences between this and the uncatalysed reaction.

III. ANALYTICAL METHODS

Partition chromatography was extensively used for the separation of reaction products. Monocarboxylic acids were tentatively identified by paper chromatography using a butanol-ammonia system (Reid and Lederer 1951) and were isolated by chromatography on silica gel.

For the separation on paper of dicarboxylic and hydroxy acids some new solvent systems were developed. A list of R_F values is given in Table 1. The general utility of systems A and B was demonstrated by the complete resolution

TABLE 1
 R_F VALUES OF DICARBOXYLIC AND HYDROXY ACIDS ON WHATMAN PAPER NO. 1

Acid	Solvent*		
	A	B	C
Malonic	0.06	0.03	—
Succinic	0.16	0.09	—
Glutaric	0.26	0.16	—
Adipic	0.40	0.30	0.09
Pimelic	0.55	0.52	0.22
Suberic	0.69	0.70	0.42
Azelaic	0.77	0.81	0.65
Sebacic	0.88	0.87	0.78
<i>meso</i> -2,3-Diethylsuccinic	0.74	0.74	0.56
<i>racemic</i> -2,3-Diethylsuccinic	0.72	0.72	0.40
2-Ethyl-3-methylglutaric	0.74	0.74	0.44
<i>p</i> -Hydroxybenzoic	0.48	—	—
2-Hydroxybutyric	0.25	—	—

* Solvents: (A) toluene-butanol-50% aqueous acetic acid, 10:1:5 (upper phase); (B) toluene-butanol-20% aqueous acetic acid, 8:1:5 (upper phase); (C) carbon tetrachloride-water-glacial acetic acid, 10:2:1 (lower phase).

into its constituents of a test mixture containing all of the homologous acids from malonic to sebacic. A wider separation of acids with 5 to 10 carbon atoms was observed using system C which also enabled the separation of 2-ethyl-3-methylglutaric and *meso*- and *racemic*-2,3-diethylsuccinic acids.

The dicarboxylic acids produced in the free-radical reactions were quantitatively estimated by titration of the fractions obtained by chromatography on silica gel using dilute sulphuric acid as the stationary phase and carbon tetrachloride-acetone mixtures as the moving phase. The isomeric 2,3-diethylsuccinic acids were separated in this way but it was not possible to resolve a mixture of 2-ethyl-3-methylglutaric and *racemic*-2,3-diethylsuccinic acids and

for a complete analysis of the reaction mixture it was necessary to titrate the acids after extraction of the spots on a paper chromatogram. None of these chromatographic methods gave indications of separating 2-ethyl-3-methylglutaric acid into its two racemic forms.

In every case the identity of the products was confirmed by comparison with authentic specimens. The *meso*- and *racemic*-2,3-diethylsuccinic acids were prepared from ethyl 2-bromobutyrate (Steinkopf, Frommel, and Leo 1941), and 2-ethyl-3-methylglutaric acid was obtained by hydrogenation and hydrolysis of diethyl 2-ethylidene-3-methylglutarate produced by condensation of ethyl crotonate in the presence of sodium ethoxide. The *p*-toluidides of a number of branched-chain acids were prepared for comparison with reaction products. The malonic ester synthesis was used for the preparation of 2-ethylvaleric, 2-ethyl-4-methylvaleric, 2-ethylcaproic, 2-propylvaleric, and 3-methylcaproic acids, while 2-ethyl-2-methylvaleric acid was obtained by carboxylation of the Grignard reagent from 3-chloro-3-methylhexane. 2-Butyroxylbutyric acid was prepared from the appropriate hydroxy acid.

IV. EXPERIMENTAL

Melting points are uncorrected. Analyses were carried out by the C.S.I.R.O. and University of Melbourne Microanalytical Laboratory.

(a) Analytical Methods

(i) *Paper Chromatography*.—Monocarboxylic acids were separated on Whatman No. 1 paper using the system 1.5*N* ammonia-butanol (1:1) for descending chromatography (Reid and Lederer 1951). Spots were visualized by spraying with bromocresol purple solution. The solvent systems employed for the separation of dicarboxylic acids are given in Table 1. Bromocresol green was used for the detection of the spots. For quantitative analyses two strips 6 in. wide were streaked with a solution of the mixture of acids and were developed with solvent system (C) to a distance of c. 18 in. After spraying with a dilute neutral solution of bromocresol green the papers were dried and the strips containing the pure acids were cut into small pieces, swirled with hot water, and titrated with potassium hydroxide solution.

(ii) *Elution Chromatography*.—For the separation of monocarboxylic acids the stationary phase was silica gel bearing 30% v/w of dilute aqueous bromocresol green, and the moving phase was *iso*-octane-acetone (10:1). Dicarboxylic acids were separated on silica gel treated with 30% v/w of 0.5*N* sulphuric acid by elution with carbon tetrachloride-acetone (10:1). Mixtures of long-chain dicarboxylic acids were resolved on the same stationary phase by elution with *iso*-octane-carbon tetrachloride mixtures. Chromatographic fractions were collected automatically and titrated with standard potassium hydroxide.

(iii) *Partition Coefficients*.—In order to evaluate the practicability of separating dicarboxylic acids by counter-current distribution the following partition coefficients were determined: for *meso*-2,3-diethylsuccinic acid in ether-water (partition coeff., $k=9$); water-benzene (k , 26); ether-benzene (1:1)-water (k , 3.2); ether-buffer pH 4.9 (k , 6.3); ether-buffer pH 5.9 (k , 1.9). For *racemic*-2,3-diethylsuccinic acid in ether-water the partition coeff. was 5.0, and for 2-ethyl-3-methylglutaric acid in ether-water the partition coeff. was 5.6.

(iv) *Adsorption Chromatography*.—Alumina for chromatography (Spence type U.G. 1) was washed with dilute hydrochloric acid and then with copious amounts of distilled water. It was dried at 150 °C and deactivated, if necessary, by shaking with 5% w/w of distilled water.

(v) *Vapour-Phase Chromatography*.—Volatile reaction products were analysed in a Griffin and George vapour-phase chromatographic apparatus. Columns were packed with "Celite" (40-80 mesh B.S.S.) bearing a stationary phase of "Silicone 30" or "Apiezon L." (1:4 w/w).

(b) Reaction of Di-*tert*-butyl Peroxide with *n*-Butyric Acid

n-Butyric acid (90 ml; b.p. 162 °C) and di-*tert*-butyl peroxide (10.0 g; b.p. 50–52 °C/90 mm) were heated under nitrogen in a vapour-bath at 116 °C for 92 hr. When the colourless reaction mixture was fractionally distilled through a short column packed with glass helices the following fractions, which were analysed by vapour-phase chromatography, were obtained:

(i) 1.9 g, b.p. 54–58 °C, of acetone, confirmed by preparation of the 2,4-dinitrophenyl-hydrazone, m.p. 127 °C.

(ii) 6.1 g, b.p. 76–82 °C, of *tert*-butanol (containing <5% of acetone) confirmed by preparation of the 3,5-dinitrobenzoate, m.p. 141 °C.

(iii) 15 g, b.p. 78 °C/40 mm, consisting mainly of *n*-butyric acid together with a small quantity of *tert*-butyl butyrate and traces of di-*tert*-butyl peroxide and *tert*-butanol. The *tert*-butyl butyrate (0.65 g) was isolated by extraction of an alkaline aqueous solution of the fraction with ether.

(iv) 64 g, b.p. 70–82 °C/30 mm, of *n*-butyric acid.

The residue was subjected to steam distillation. The distillate (800 ml), which contained oily droplets of an insoluble acid, gave spots with R_F values 0.3 (butyric acid) and 0.73 when chromatographed on paper. Extraction of the steam distillate with hexane yielded the crude acid (0.34 g) with R_F 0.74, which was purified by partition chromatography on tinted silica gel. The product had an infra-red spectrum almost identical with that of 2-ethyl-4-methylvaleric acid. Its structure was confirmed by preparation of the *p*-toluidide which was chromatographed on alumina and then crystallized from pentane in needles, m.p. 111 °C, identical with authentic 2-ethyl-4-methylvalero-*p*-toluidide.

The aqueous residue from the steam distillation was extracted with an equal volume of benzene, and the extract was divided into neutral (0.7 g) and acid fractions (A, 0.9 g) by treatment with aqueous potassium bicarbonate. After separation of the benzene layer the aqueous portion was extracted with ether (4 × 100 ml). Evaporation of the solvent yielded a colourless, partly-crystalline residue (B, 6.46 g). Finally, the aqueous solution was continuously extracted with ether for 48 hr, and there was then obtained a colourless solid (C, 0.23 g).

Fraction A was a light brown gum with equiv. wt. 152 (fading end-point). Paper chromatography (ammonia–butanol) showed spots with R_F values, 0.54 (2-butyroxybutyric acid ?), 0.73, and 0.05. When solvent system A was employed spots were observed with R_F 0.9 (C_{12} dicarboxylic acid ?) and 0.74. After hydrolysis of a drop of fraction A with alcoholic potassium hydroxide, butyric acid was detected, and paper chromatography (system A) revealed a new spot with R_F 0.23 (2-hydroxybutyric acid ?).

Fraction B had equiv. wt. 98. Paper chromatography (system A) showed spots with R_F values 0.9, 0.64, and 0.40, while with system C spots were detected with R_F values 0.84 (C_{12} dicarboxylic acids ?), 0.56 (*meso*-2,3-diethylsuccinic acid), 0.44 (2-ethyl-3-methylglutaric acid), 0.41 (*racemic*-2,3-diethylsuccinic acid), and 0.10 (unidentified). Crystallization of fraction B from water yielded 1.88 g of pure *meso*-2,3-diethylsuccinic acid, m.p. 200–204 °C, and a further 0.24 g of crude acid, m.p. 192–196 °C, was obtained after concentration of the mother liquor. The mother liquor was then extracted with ether, the ether extract was evaporated to dryness, and the residue was crystallized from hexane–benzene. Crude *racemic*-2,3-diethylsuccinic acid (0.98 g), m.p. 122–129 °C, was obtained and was purified by recrystallization.

Evaporation of the mother liquor yielded a gummy residue (D, 3.20 g) which was analysed by the methods described in the first part of the experimental section, and was thus estimated to contain 0.46 g of *meso*-2,3-diethylsuccinic acid, 1.40 g of *racemic*-2,3-diethylsuccinic acid, and 0.32 g of 2-ethyl-3-methylglutaric acid.

A sample of D (1.72 g) was treated in the usual way with *p*-phenylphenacyl bromide. When the crude product (6.56 g) was dissolved in benzene and chromatographed on alumina pure specimens of the *p*-phenylphenacyl esters of 2-ethyl-3-methylglutaric and *meso*- and *racemic*-2,3-diethylsuccinic acids were obtained. An unidentified compound, which was eluted with ether-

benzene (1:9), crystallized from methanol in rosettes of needles, m.p. 116–117 °C (Found: C, 72.0; H, 6.1%. Calc. for $C_{22}H_{22}O_8$: C, 72.1; H, 6.1%).

Fraction C on paper chromatography (system A) gave spots with R_F values 0.18 and 0.23. No acids were identified.

(c) *Reaction of Di-tert.-butyl Peroxide with Ethyl n-Butyrate*

Ethyl butyrate (90 ml; b.p. 119–120 °C) and di-tert.-butyl peroxide (8.5 g) were heated under nitrogen in a vapour-bath at 116 °C for 7 days. The colourless reaction mixture was then distilled through a short fractionating column. Acetone and *tert.*-butanol were the only volatile products. After removal of the excess of ethyl butyrate the residual material was distilled under reduced pressure and there was then obtained a mixture of dimers (A, 5.5 g), b.p. 124–140 °C/20 mm, and a gummy residue (B, 3.6 g).

Fraction A was refluxed with aqueous potassium hydroxide (70 ml; 10%) for 14 hr by which time all the oil had dissolved. The reaction mixture was then acidified with dilute sulphuric acid and steam distilled until the distillate was no longer acidic. The steam distillate contained butyric acid together with a trace of an unsaturated acid, R_F 0.47 (caproic acid has R_F 0.51). By titration of 5.0 ml aliquots of steam distillate with standard potassium hydroxide solution the total amount of butyric acid was estimated to be 0.65 g. The aqueous residue from the steam distillation was extracted with ether (4 × 100 ml) and there was obtained a solid mixture of acids (3.49 g) which was found by paper chromatography (system C) to contain *meso*- and *racemic*-2,3-diethylsuccinic and 2-ethyl-3-methylglutaric acids in the ratio 5:5:1. A sample (0.43 g) of the acid mixture was treated in the usual way with *p*-phenylphenacyl bromide and the resultant crude esters were washed with hot ethanol and water. The washings contained the *p*-phenylphenacyl ester of 2-ethyl-3-methylglutaric acid (80 mg) which was purified by crystallization from ether. The insoluble material (1.25 g) was separated by fractional crystallization from chloroform and ethanol into the pure *p*-phenylphenacyl esters of *meso*- and *racemic*-2,3-diethylsuccinic acids.

The residue B was analysed by the same method as fraction A. It contained an unidentified neutral material (0.7 g) which resisted hydrolysis. The amount of butyric acid in the steam distillate was 0.34 g, and 1.9 g of an acid mixture was extracted from the aqueous residue with ether. The acid mixture contained the three dibasic acids previously obtained plus two unidentified acids with R_F values of 0.1 (system C) and 0.36 (butanol-ammonia).

(d) *Cupric Chloride-Catalysed Reaction of Di-tert.-butyl Peroxide with n-Butyric Acid*

n-Butyric acid (90 ml), di-tert.-butyl peroxide (10 g), and cupric chloride dihydrate (0.25 g) were heated under nitrogen in a vapour-bath at 116 °C for 4 days. The reaction mixture was then distilled through a short fractionating column yielding acetone, *tert.*-butanol, and unchanged butyric acid. The residue was shaken with water (100 ml) and benzene (100 ml) and the benzene extract was divided into neutral (0.58 g) and acid (A, 2.97 g) fractions by treatment with aqueous potassium bicarbonate. The aqueous phase was then extracted with ether and an oily acid (B, 2.62 g) was obtained. Finally the aqueous phase was extracted continuously with ether to yield a solid acid (0.9 g).

The benzene-soluble acid (A) when chromatographed on paper gave spots with R_F values 0.46, 0.55, 0.62 (butanol-ammonia), and 0.81 (system A). All of these spots decolourized potassium permanganate and hence contained unsaturated or hydroxy acids. The infra-red spectrum showed peaks at 1786 and 1739 cm^{-1} . When a sample (1.12 g) of the acid was treated in the usual way with *p*-phenylphenacyl bromide and the crude product was chromatographed on alumina there were obtained the *p*-phenylphenacyl ester of butyric acid (0.38 g), an ester of m.p. 59–60 °C (needles from pentane) (Found: C, 71.8; H, 6.6%. Calc. for $C_{22}H_{22}O_8$: C, 71.7; H, 6.6%), and a second ester, m.p. 127–128 °C (prisms from ether) (Found: C, 77.1; H, 6.1%. Calc. for $C_{26}H_{26}O_8$: C, 76.9; H, 6.1%). From another portion of fraction A there was obtained a *p*-toluimide which crystallized from hexane in needles, m.p. 87–88 °C (Found: C, 69.2; H, 7.3%. Calc. for $C_{18}H_{18}O_3N$: C, 68.9; H, 7.3%).

The ether-soluble acid (B) was a pale yellow oil. When chromatographed on paper it showed spots with R_F values 0.24 (butanol-ammonia) and 0.57 (system A). The latter spot decolourized

potassium permanganate solution. The crude acid itself also decolorized potassium permanganate but it showed no reaction with bromine water, ammoniacal silver nitrate, or ferric chloride solution. There was a broad and intense adsorption peak in the infra-red between 1786 and 1715 cm^{-1} . Chromatography on alumina of the crude *p*-phenylphenacyl ester yielded a compound which crystallized from methanol in needles, m.p. 116–117°C (Found: C, 72.0; H, 6.1%. Calc. for $\text{C}_{22}\text{H}_{22}\text{O}_3$: C, 72.1; H, 6.1%).

(e) Preparation of Reference Compounds

(i) *2-Ethyl-3-methylglutaric Acid*.—A suspension of sodium ethoxide (from 9.2 g of Na) in anhydrous ether (150 ml) was cooled in a dry-ice bath while a solution of ethyl crotonate (40 g; b.p. 139°C) in ether (100 ml) was added with stirring. After the addition (1 hr) the mixture was stirred under reflux for 3 hr, then cooled in ice, and acidified with acetic acid (20 ml). After an excess of 6*N* sulphuric acid had been added the ether layer was separated, washed with aqueous sodium carbonate and with water, and dried. Distillation of the residue after removal of the solvent yielded diethyl 2-ethylidene-3-methylglutarate (24 g; 60%), b.p. 136–138°C/18 mm.

When the unsaturated ester (24 g) was dissolved in ethanol (150 ml; 96%) and hydrogenated over 10% palladium on charcoal (2.0 g) at atmospheric pressure the theoretical volume of hydrogen was adsorbed in 4.5 hr. After filtration of the mixture and removal of the solvent by distillation there remained crude diethyl 2-ethyl-3-methylglutarate (24.2 g).

The crude ester (10.0 g) was refluxed for 16 hr with potassium hydroxide (10 g) in ethanol (200 ml; 50%). Most of the solvent was removed by distillation under reduced pressure and the residue, after acidification with 6*N* sulphuric acid, was extracted with ether. The residue from the ether extract when crystallized from ether-hexane yielded a mixture of the *racemic* forms of 2-ethyl-3-methylglutaric acid (6.7 g; 87%), m.p. 82–87°C, equiv. wt. 88. Repeated crystallization from ether-hexane produced one isomer, m.p. 97–99°C (Found: C, 55.2; H, 8.1%. Calc. for $\text{C}_9\text{H}_{16}\text{O}_4$: C, 55.2; H, 8.1%).

The *p*-phenylphenacyl ester prepared from the mixture of *racemic* acids crystallized from ether in rods, m.p. 90–92°C (Found: C, 76.9; H, 6.3%. Calc. for $\text{C}_{28}\text{H}_{34}\text{O}_6$: C, 76.9; H, 6.1%).

(ii) *meso- and racemic 2,3-Diethylsuccinic Acids*.—Diethyl 2,3-diethylsuccinate was prepared from ethyl-2-bromobutyrate by the method of Steinkopf, Frommel, and Leo (1941). The ester (12.7 g) was refluxed with potassium hydroxide (10 g) in ethanol (30 ml; 70%) for 8 hr, and the mixture was then acidified with 6*N* sulphuric acid and diluted with water (150 ml). The alcohol was removed by distillation, and upon cooling the aqueous residue a precipitate of crude *meso*-2,3-diethylsuccinic acid (3.7 g), m.p. 192–194°C, was obtained. Extraction of the mother liquor with ether yielded a further quantity (4.2 g) of crude acid which was separated into the two isomeric forms by fractional crystallization from acetone-carbon tetrachloride. Pure *meso*-2,3-diethylsuccinic acid was obtained as rods, m.p. 204°C (Found: C, 55.4; H, 8.1%. Calc. for $\text{C}_8\text{H}_{14}\text{O}_4$: C, 55.2; H, 8.1%), and the *racemic* form crystallized from ether-hexane in needles, m.p. 135°C (Found: C, 55.3; H, 8.1%).

The *p*-phenylphenacyl ester of the *meso* acid crystallized from chloroform or toluene in needles, m.p. 228°C (Found: C, 77.1; H, 6.1%. Calc. for $\text{C}_{28}\text{H}_{34}\text{O}_6$: C, 76.9; H, 6.1%), and the *p*-bromophenacyl ester separated from acetone in needles, m.p. 151–152°C (Found: C, 50.9; H, 4.3%. Calc. for $\text{C}_{24}\text{H}_{24}\text{O}_6\text{Br}_2$: C, 50.7; H, 4.2%).

The *racemic* acid yielded a *p*-phenylphenacyl ester (rods from ethyl acetate), m.p. 185°C (Found: C, 76.6; H, 6.1%), and a *p*-bromophenacyl ester (needles from methanol), m.p. 121–122°C (Found: C, 50.7; H, 4.3%).

(iii) *2-Ethyl-2-methylvaleric Acid*.—3-Methylhexan-3-ol (b.p. 62°C/25 mm), prepared by reaction of ethylmagnesium iodide with pentan-2-one, was saturated with dry hydrogen chloride (ice cooling) and allowed to stand overnight. 3-Chloro-3-methylhexane, b.p. 76°C/80 mm, was obtained in 90% yield. The Grignard reagent from the chloro compound (18 g) in ether (200 ml) was sealed in an autoclave with solid carbon dioxide (100 g). The pressure inside the reaction vessel rose rapidly to 30 atm then slowly decreased. After standing 48 hr at room temperature the autoclave was opened and the reaction mixture was poured into cold dilute

hydrochloric acid. Distillation of the ether layer yielded 2-ethyl-2-methylvaleric acid (9.9 g; 50%), b.p. 132 °C/25 mm. A sample of the acid was converted by treatment with oxalyl chloride to the acid chloride and hence to the *p*-toluicide, which crystallized from hexane in needles, m.p. 92 °C (Found: C, 77.1; H, 9.9; N, 6.2%. Calc. for $C_{15}H_{23}ON$: C, 77.2; H, 9.9; N, 6.0%).

(iv) *2-Ethylvaleric Acid*.—Diethyl malonate was converted to diethyl ethylpropylmalonate by successive alkylation with ethyl and propyl bromides according to standard procedure (Adams and Kamm 1941). Hydrolysis of the ester with 50% aqueous potassium hydroxide followed by decarboxylation of the substituted malonic acid at 180 °C yielded 2-ethylvaleric acid, b.p. 118–120 °C/20 mm. The *p*-toluicide crystallized from hexane in needles, m.p. 129 °C.

(v) *2-Ethylcaproic Acid*.—Diethyl ethylmalonate was alkylated with *n*-butyl bromide and the product was converted to the required acid (b.p. 102–106 °C/4 mm) as above. The *p*-toluicide crystallized from aqueous methanol in needles, m.p. 107 °C (Found: C, 77.2; H, 9.9; N, 5.8%. Calc. for $C_{15}H_{23}ON$: C, 77.2; H, 9.9; N, 6.0%).

(vi) *2-Propylvaleric Acid*.—Diethyl dipropylmalonate, formed by dialkylation of diethyl malonate with *n*-propyl bromide was converted in the usual way to 2-propylvaleric acid, b.p. 118–120 °C/10 mm. The *p*-toluicide crystallized from hexane in needles, m.p. 154 °C (Found: C, 77.5; H, 10.1; N, 6.0%. Calc. for $C_{15}H_{23}ON$: C, 77.2; H, 9.9; N, 6.0%).

(vii) *2-Ethyl-4-methylvaleric Acid*.—The required acid (b.p. 84–86 °C/2 mm) was prepared by the malonic ester synthesis using *isobutyl* bromide and ethyl iodide. The *p*-toluicide crystallized from pentane in needles, m.p. 111 °C (Found: C, 77.1; H, 9.9; N, 5.9%. Calc. for $C_{15}H_{23}ON$: C, 77.2; H, 9.9; N, 6.0%).

(viii) *3-Methylcaproic Acid*.—The required acid (b.p. 101–102 °C/10 mm) was prepared by the malonic ester synthesis using 2-bromopentane. The *p*-toluicide had m.p. 73 °C (Found: C, 76.6; H, 9.4; N, 6.4%. Calc. for $C_{14}H_{21}ON$: C, 76.7; H, 9.7; N, 6.4%).

(ix) *2-Butyroxylbutyric Acid*.—2-Hydroxybutyric acid (8.9 g), butyric anhydride (20 ml), and pyridine (5 ml) were dissolved in benzene and allowed to stand at room temperature overnight. The mixture was then refluxed for 30 min, cooled, and poured into water. Distillation of the benzene layer under reduced pressure yielded 2-butyroxylbutyric acid, b.p. 106–108 °C/2.5 mm, n_D^{20} 1.4298 (Found: C, 55.5; H, 8.4%. Calc. for $C_8H_{14}O_4$: C, 55.2; H, 8.1%). The *p*-phenylphenacyl ester crystallized from pentane in laths, m.p. 53–54 °C (Found: C, 71.6; H, 6.6%. Calc. for $C_{22}H_{18}O_3$: C, 71.7; H, 6.6%).

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BROMINATION OF 2,7-DIHYDROXYNAPHTHALENE

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Summary

Bromination of 2,7-dihydroxynaphthalene gives a mixture of two dibromo derivatives which are now identified as the 1,6- and 1,3-isomers. Reduction of these compounds gives the new 3-bromo-2,7-dihydroxynaphthalene. Similar reduction of 1,3,6-tribromo-2,7-dihydroxynaphthalene gives the previously unknown 3,6-dibromo-2,7-dihydroxynaphthalene. After methylation this is readily converted into 2,7-dimethoxynaphthalene-3,6-dicarboxylic acid by carbonation of the lithium derivative. It has not been possible to substantiate claims that 2,7-dihydroxynaphthalene and its dimethyl ether give 1,3,6,8-tetrabromo derivatives.

I. INTRODUCTION

Papers by Bell, Gibson, and Wilson (1956) and by Buu-Hoi and Lavit (1956) have reviewed the confused information relating to the substitution reactions of 2,7-dihydroxynaphthalene. Consideration was still given to earlier conclusions that chlorination occurs in positions 1 and 8, and that bromine substitutes in positions 3 and 6. On the other hand some more recent observations were not fully appreciated. Subsequently Wilson (1958) noted that the results of Adams *et al.* (1942), together with those of Sunthakar and Gilman (1951) established fairly definitely that the first bromine atom enters the 1-position. This conclusion was also supported by some of the observations reported by Buu-Hoi and Lavit (1956). Wilson has also concluded that the dichloro and dibromo derivatives have the 1,6-orientation. In the meantime a different approach to this problem was briefly reported (Cooke, Johnson, and Owen 1957) and full details of these and other experiments are now presented.

II. BROMINATION PRODUCTS

It is now established that the reaction of 2,7-dihydroxynaphthalene with two molecules of bromine produces two dibromo derivatives. These cannot be separated by crystallization from the solvents usually employed and it is evident that the material melting near 155 °C, which has been described by other workers, is in fact a mixture. The two isomers are separated by chromatography; the major component (about 73 per cent. of the mixture) has m.p. 162–163 °C, and the minor component melts at 186–187 °C. On reduction with stannous bromide or acidified potassium iodide both these isomers lose one atom of bromine and produce a new monobromo-2,7-dihydroxynaphthalene (m.p. 189–190 °C). As the previously known isomer is readily reduced to 2,7-dihydroxynaphthalene under the same conditions its structure is confirmed as 1-bromo-2,7-dihydroxy-

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naphthalene and the new product must be the 3-bromo derivative. The two dibromodihydroxynaphthalenes also transfer one bromine atom to β -naphthol dissolved in acetic acid and hydrobromic acid. The products are 1-bromo-2-naphthol and the same new 3-bromo-2,7-dihydroxynaphthalene.

These results suggest that the two dibromo derivatives are the 1,3- and 1,6-isomers. There remains, however, the possibility that one might be the 1,8-isomer and that rearrangement might precede reduction. This had to be considered in view of the claim by Bell, Gibson, and Wilson (1956) that 2,7-dihydroxynaphthalene is easily tetrabrominated, and their description of 1,3,6,8-tetrabromo-2,7-dimethoxynaphthalene—produced by further bromination of the dibromodimethoxynaphthalene. These results implied that there is no great steric hindrance to the introduction of two bromine atoms in the 1- and 8-positions.

The dibromodihydroxynaphthalene with melting point 186–187 °C can be isomerized to the compound with melting point 162–163 °C by heating with hydrobromic acid in acetic acid. However, the rearrangement appears to be considerably slower than the reductions described above and no 2,7-dihydroxynaphthalene was detected among the reduction products. It therefore seemed unlikely that the unstable isomer could be 1,8-dibromo-2,7-dihydroxynaphthalene. Furthermore, despite several attempts, we have not been able to prepare tetrabromo derivatives of 2,7-dihydroxynaphthalene or its dimethyl ether.

The structures of the two dibromodihydroxynaphthalenes were finally established by the following experiments. The less stable minor product readily gives a monomethyl ether which has been degraded to 3,5-dibromo-4-methoxyphthalic acid. It is therefore 1,3-dibromo-2,7-dihydroxynaphthalene. Furthermore by reduction of the known tribromo-2,7-dihydroxynaphthalene with tin and hydrobromic acid the hitherto unknown 3,6-dibromo-2,7-dihydroxynaphthalene has been prepared. The dimethyl ether of this product is easily converted, by means of the lithium derivative, into 2,7-dimethoxynaphthalene-3,6-dicarboxylic acid. Sunthakar and Gilman (1951) prepared this acid in low yield by direct metalation of 2,7-dimethoxynaphthalene followed by carbonation. It is therefore evident that the remaining reasonable structure, 1,6-dibromo-2,7-dihydroxynaphthalene, must be assigned to the major dibromination product of melting point 162–163 °C.

As the dibromination of 2,7-dihydroxynaphthalene gives two isomers it is necessary to re-examine the relationship of the hydroxy compounds to their methyl ethers. It is now established that the previously described dibromo-2,7-dimethoxynaphthalene is the pure 1,6-isomer. The 1,3-isomer is much more soluble in this case and it has evidently always been easily removed from the main product and discarded in the mother liquors. Thus the formation of two brominated naphthoquinones by oxidation of this material (Wilson 1958) is evidently not due to inhomogeneity. However it is now believed (Wilson, personal communication) that both these products are 1,4-quinones.

In view of the demonstrated reactivity of the α -bromine atoms in brominated 2,7-dihydroxynaphthalenes, and the failure to obtain tetrabromo derivatives in this investigation, the reported relationship of the dichloro to the dibromo

derivatives seems uncertain. As even tribromo-2,7-dihydroxynaphthalene is rather unstable the identity of the alleged dibromodichloro derivatives (Bell, Gibson, and Wilson 1956) seems doubtful. Finally it seems unlikely that any derivative of 2,7-dihydroxynaphthalene has been prepared with two bromine atoms in the 1- and 8-positions. It is significant that Sunthakar and Gilman (1951) were not able to introduce more than one bromine atom into 2,7-dihydroxynaphthalene-3,6-dicarboxylic acid and its dimethyl ether.

III. EXPERIMENTAL

Melting points are corrected and were observed in Pyrex capillaries. Microanalyses by Dr. K. W. Zimmermann and assistants.

(a) *1-Bromo-2,7-dihydroxynaphthalene*.—This compound was prepared as described by Bell, Gibson, and Wilson (1956). Careful chromatography showed that it was homogeneous. After crystallization from aqueous ethanol it had m.p. 134–135 °C.

(b) *Reduction of 1-Bromo-2,7-dihydroxynaphthalene*.—The monobromo compound (180 mg) was dissolved in glacial acetic acid (5 c.c.) containing excess stannous bromide (from 100 mg tin) and hydrobromic acid. The solution was heated on the water-bath for 20 min; water was then added and the product was extracted with ether. The residue from the ethereal solution was crystallized from water to give 2,7-dihydroxynaphthalene (110 mg), m.p. and mixed m.p. 189–190 °C.

(c) *Dibromination of 2,7-Dihydroxynaphthalene*.—The method was essentially the same as described by Bell, Gibson, and Wilson (1956). Bromine (6 g) was passed with a stream of carbon dioxide into a stirred solution of 2,7-dihydroxynaphthalene (3 g) in glacial acetic acid (60 c.c.) during 3 hr. The mixture was finally heated on a water-bath for 15 min and then poured into water. The recovered solid was dried and the products were separated by chromatography of a benzene solution on a column of silica. The *1,6-dibromo-2,7-dihydroxynaphthalene* (3 g) was eluted first and crystallized from benzene or aqueous acetic acid in needles, m.p. 162–163 °C (Found: C, 37.5; H, 2.5; Br, 49.9%. Calc. for $C_{16}H_8O_2Br_2$: C, 37.8; H, 1.9; Br, 50.3%).

The second product from the silica column was crystallized from benzene or aqueous ethanol to give *1,3-dibromo-2,7-dihydroxynaphthalene* (1.3 g) as needles, m.p. 186–187 °C (Found: C, 37.9; H, 2.1; Br, 49.9%. Calc. for $C_{16}H_8O_2Br_2$: C, 37.8; H, 1.9; Br, 50.3%).

Methylation of the first of these two pure products with excess diazomethane in ether, or with dimethyl sulphate and potassium carbonate in acetone, gave *1,6-dibromo-2,7-dimethoxynaphthalene*, needles from light petroleum, m.p. 126–127 °C, or from methanol, m.p. 130–131 °C (lit. m.p. 131 °C). Similarly the second product gave *1,3-dibromo-2,7-dimethoxynaphthalene* which crystallized from aqueous methanol in needles, m.p. 80–81 °C (Found: C, 41.7; H, 3.0; Br, 46.4; OMe, 17.5%. Calc. for $C_{12}H_{10}O_2Br_2$: C, 41.6; H, 2.9; Br, 46.2; 2 × OMe, 17.9%).

In another experiment the crude mixture of dibromodihydroxynaphthalenes was methylated with excess diazomethane and the methyl ethers were separated by crystallization and chromatography on alumina. The 1,6- and 1,3-dibromodimethoxynaphthalenes were obtained in yields of 55 and 19% respectively.

(d) *3-Bromo-2,7-dihydroxynaphthalene*.—Either of the above dibromodihydroxynaphthalenes (5 g) in acetic acid (150 c.c.) was reduced with freshly prepared stannous bromide (from 5 g tin) and hydrobromic acid. The mixture was heated on the water-bath for 20 min, water was then added, and the product was extracted with ether. The extract was washed with aqueous sodium bicarbonate, dried and evaporated. The residue was purified by chromatography of a benzene solution on silica. The product was eluted with benzene containing 3% ethanol. The same compound was obtained from both isomers and crystallization from benzene gave *3-bromo-2,7-dihydroxynaphthalene* as needles, m.p. 191–192 °C (Found: C, 50.0; H, 3.0; Br, 33.5%. Calc. for $C_{16}H_9O_2Br$: C, 50.2; H, 2.9; Br, 33.5%). Methylation with dimethyl sulphate and potassium carbonate in acetone gave *3-bromo-2,7-dimethoxynaphthalene* which crystallized from light petroleum (b.p. 60–70 °C) in prisms, m.p. 108–109 °C (Found: C, 54.3; H, 4.2; O, 12.3; OMe, 22.4%. Calc. for $C_{12}H_{11}O_2Br$: C, 53.9; H, 4.2; O, 11.9; 2 × OMe, 23.2%).

The dibromodihydroxynaphthalenes (0.3 g) were also reduced by refluxing for 1 hr with potassium iodide (0.5 g) in water (50 g.c.) and acetic acid (0.5 c.c.).

A mixture of dibromodihydroxynaphthalene (0.5 g), β -naphthol (0.2 g), hydrobromic acid (48% ; 0.5 c.c.), and acetic acid (3 c.c.) was heated for 10 min on the water-bath. Water was added, the mixture was extracted with ether, and the recovered products were separated by chromatography in benzene over silica gel. Part of the reactants was recovered, together with 1-bromo-2-naphthol and 3-bromo-2,7-dihydroxynaphthalene.

(e) *Isomerization of 1,3-Dibromo-2,7-dihydroxynaphthalene*.—The dibromo compound (m.p. 186–187 °C ; 50 mg) in acetic acid (4 c.c.) was heated on the water-bath for 15 min with hydrobromic acid (48% ; 0.05 c.c.). Water was added and the ethereal extract, after washing with sodium bicarbonate, gave a mixture of products which was separated by chromatography in benzene over silica. The first fraction gave 1,6-dibromo-2,7-dihydroxynaphthalene (m.p. 162–163 °C ; 20 mg) and the second fraction was unchanged isomer.

(f) *Bromination of 3-Bromo-2,7-dihydroxynaphthalene*.—Treatment with one molecule of bromine gave only 1,6-dibromo-2,7-dihydroxynaphthalene, m.p. and mixed m.p. 162–163 °C.

(g) *1,3-Dibromo-7-hydroxy-2-methoxynaphthalene*.—The reaction of 1,3-dibromo-2,7-dihydroxynaphthalene with one molecular proportion of diazomethane in ether gave a monomethyl ether. This was extracted with aqueous sodium hydroxide, recovered by acidification, and purified by chromatography in benzene over silica. The 1,3-dibromo-7-hydroxy-2-methoxynaphthalene crystallized from benzene–light petroleum in needles, m.p. 142–143 °C (Found : OMe, 9.3%. Calc. for $C_{11}H_8O_2Br_2$: OMe, 9.4%).

(h) *Oxidation of 1,3-Dibromo-7-hydroxy-2-methoxynaphthalene*.—The monomethyl ether (0.3 g) was dissolved in aqueous sodium hydroxide (8% ; 25 c.c.) and heated on the water-bath for 3 hr while solid potassium permanganate (2 g) was gradually added with stirring. The mixture was then refluxed for a further hour and finally sodium sulphite and hydrochloric acid were added to reduce the manganese dioxide. The solution was saturated with sodium chloride and continuously extracted with ether. The solid residue from the ether gave a fluorescein reaction. It was sublimed in a high vacuum and esterified with excess diazomethane in ether. After chromatography in benzene over silica the ester crystallized from light petroleum (b.p. 55–70 °C) as needles, m.p. 79–80 °C. It was identical (mixed m.p. and infrared spectrum) with a sample of dimethyl 3,5-dibromo-4-methoxyphthalate prepared as described below.

(i) *Synthesis of Dimethyl 3,5-Dibromo-4-methoxyphthalate*.—Dimethyl 4-hydroxyphthalate was prepared essentially as described by Girardet (1931) for the diethyl ester. The crude product (0.3 g) was allowed to react for 2 days with bromine (0.3 g) in acetic acid (7 c.c.). Water was then added and the product was treated with excess diazomethane in ether. The dimethyl 3,5-dibromo-4-methoxyphthalate crystallized from light petroleum in needles, m.p. 79–80 °C (Found : C, 34.9 ; H, 2.9 ; Br, 41.7 ; OMe, 24.8%. Calc. for $C_{11}H_8O_4Br_2$: C, 34.6 ; H, 2.6 ; Br, 41.8 ; OMe, 24.4%).

(j) *1,3,6-Tribromo-2,7-dihydroxynaphthalene*.—Bromine (9 g) in acetic acid (60 c.c.) was slowly added to 2,7-dihydroxynaphthalene (3 g) in acetic acid (30 c.c.). The product precipitated by water was crystallized from acetic acid, and from aqueous ethanol, and was then purified further by chromatography in benzene over silica. Finally it crystallized from aqueous ethanol in needles, m.p. 206.5–207.5 °C (Found : C, 30.7 ; H, 1.6 ; Br, 59.5%. Calc. for $C_{10}H_6O_2Br_3$: C, 30.3 ; H, 1.3 ; Br, 60.4%). This compound is unstable and turns pink on standing. Ioffe and Fedorova (1936) report m.p. 205 °C.

The dimethyl ether was prepared by the action of excess diazomethane in ether. It crystallized from ethanol in needles, m.p. 173–174 °C (Found : C, 34.1 ; H, 2.4 ; Br, 56.1 ; OMe, 14.2%. Calc. for $C_{12}H_{10}O_2Br_2$: C, 33.9 ; H, 2.1 ; Br, 56.4 ; 2×OMe, 14.6%). Bell, Gibson, and Wilson (1956) report m.p. 173 °C.

(k) *3,6-Dibromo-2,7-dihydroxynaphthalene*.—Bromine (26 g) in acetic acid (50 c.c.) was added during 20 min to 2,7-dihydroxynaphthalene (6.5 g) in acetic acid (150 c.c.). The mixture was diluted with water (20 c.c.) and then boiled under a reflux condenser while tin (10 g) was gradually added. The heating was continued for 4 hr and the mixture was then cooled to 50 °C, filtered, and diluted with water. The precipitated product (11 g, m.p. 186–190 °C) crystallized

from aqueous acetic acid and from benzene (charcoal) to give 3,6-dibromo-2,7-dihydroxynaphthalene as needles, m.p. 189–190 °C (Found: C, 37.7; H, 2.0; Br, 50.5%. Calc. for $C_{10}H_6O_2Br_2$: C, 37.8; H, 1.9; Br, 50.3%). This product was also obtained by reduction of the tribromo compound with stannous chloride.

Methylation with excess diazomethane in ether, or with dimethyl sulphate and potassium carbonate in acetone, gave 3,6-dibromo-2,7-dimethoxynaphthalene which was purified by chromatography on alumina and crystallization from benzene–light petroleum or from ethanol. It formed needles, m.p. 176.5–177 °C (Found: C, 41.6; H, 3.1; Br, 46.3; OMe, 17.5%. Calc. for $C_{12}H_{10}O_2Br_2$: C, 41.6; H, 2.9; Br, 46.2; 2×OMe, 17.9%).

(l) 2,7-Dimethoxynaphthalene-3,6-dicarboxylic Acid.—To a filtered solution of *n*-butyl lithium (from 0.86 g lithium) in ether (30 c.c.) a solution of 3,6-dibromo-2,7-dimethoxynaphthalene (3.5 g) in ether (125 c.c.) and benzene (50 c.c.) was added during 10 min and the mixture was stirred for a further period of 10 min. It was then poured over powdered solid carbon dioxide (50 g) and allowed to stand overnight. Dilute hydrochloric acid was then added and the solid product (2.1 g; 77%) was collected by filtration and purified by treatment with charcoal in aqueous sodium carbonate solution. After reprecipitation with hydrochloric acid it was crystallized from glacial acetic acid to give very pale yellow needles, m.p. 276–279 °C (decomp.), in a bath preheated to 271 °C. (The melting point depends on the rate of heating.) Sunthakar and Gilman (1951) report m.p. 271–272 °C (Found: C, 60.7; H, 4.3; OMe, 21.9%. Calc. for $C_{14}H_{12}O_6$: C, 60.9; H, 4.3; 2×OMe, 22.6%). The dimethyl ester was prepared by the action of excess diazomethane in ether–methanol. After sublimation in a high vacuum the product crystallized from benzene–light petroleum in plates, m.p. 157–158.5 °C (Found: C, 63.0; H, 5.2; OMe, 39.4%. Calc. for $C_{16}H_{14}O_6$: C, 63.2; H, 5.3; 4×OMe, 40.8%).

(m) Attempted Preparation of Tetrabromo Derivatives.—Several attempts to substitute 2,7-dihydroxynaphthalene with four atoms of bromine gave only the 1,3,6-tribromo derivative. When the crude reaction product was methylated only 1,3,6-tribromo-2,7-dimethoxynaphthalene was isolated. This compound (500 mg) in glacial acetic acid (10 c.c.) was refluxed for 3 hr with bromine (285 mg). The mixture was then poured into water, warmed to coagulate the precipitate, and the product was purified by chromatography on alumina to give 400 mg of unchanged starting material. After two crystallizations it melted at 173.5–174.5 °C alone or mixed with authentic 1,3,6-tribromo-2,7-dimethoxynaphthalene. No other product could be isolated.

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THE CHEMISTRY OF SUGAR-CANE WAX*

I. THE NATURE OF SUGAR-CANE WAX

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Summary

Distillation of sugar-cane cuticle wax under reduced pressure gives a high yield of long-chain aldehydes, which are considered to occur in the wax in polymeric form. The products obtained from the wax under normal saponification conditions are apparently produced from the aldehydes by a Cannizzaro reaction, and by aldol condensation with subsequent dehydration. The cuticle wax also contains hydrocarbons and free alcohols and acids, but there is no conclusive evidence for the presence of esters.

I. INTRODUCTION

Although there is an extensive literature on the properties of the sugar-cane wax recovered as a by-product in the sugar industry, little attention has been paid to the chemical study of sugar-cane cuticle wax as it occurs on the plant. Thus Balch (1947) compiled much information on the properties of refined sugar-cane wax (i.e. wax extracted from filter-cake "mud" and fractionated with solvents to remove insoluble resin and oily components), and Whyte and Hengeveld (1950) published a partial analysis of the more soluble portion extracted from the crude mud wax, showing the presence of phytosterols and some of the commonly occurring fatty acids. Wijnberg (1909) claimed that the main component of the cuticle wax itself is *n*-triacontanol, but Kreger (1948) considered from X-ray evidence that *n*-octacosanol is present.

More recently Horn and Matic (1957) made a fuller examination of the cuticle wax from a South African variety of sugar-cane. After treatment under saponification conditions they obtained a low yield of acids (15.5 per cent.) and a large unsaponifiable fraction from which they separated *n*-octacosanol by distillation of its acetate in a molecular still, followed by distillation in a spinning band column. However a large part of the unsaponifiable fraction did not distil in a molecular still, and a spectroscopic study suggested that it contained ketones and conjugated ketones. Horn and Matic considered some of these unidentified compounds to be artefacts produced during the saponification of the wax.

II. EXAMINATION OF CUTICLE WAX

A study has now been made of specimens of sugar-cane cuticle wax collected in Queensland from ripe unburnt cane of variety Pindar, at four Sugar Experiment Stations (Gordonvale, Bundaberg, Ayr, Mackay). The waxes from these four

* Studies in Waxes. XV. For previous paper see Downing, D. T., Kranz, Z. H., and Murray, K. E. (1960).—*Aust. J. Chem.* **13**: 80.

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sources were closely similar in properties (Table 1, Section III). In contrast to the wax obtained from filter-cake mud, these waxes contained no phytosterols (Liebermann-Burchard test).

The ultraviolet absorption of the sugar-cane cuticle wax is negligible, showing the absence of any conjugated carbonyl compounds and of the trienoic acids reported by Horn and Matic. The infra-red absorption spectrum shows the presence of free alcohols, and has a band at 1715 cm^{-1} (Nujol) in the carbonyl region, which must be at least partly attributed to the free acids in the wax.

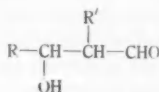
Heating the cuticle wax with potassium hydroxide in ethanol gives only a low yield of acids (Table 1, Section III). The remainder is separated by chromatography on alumina into alcohols (*c.* 40 per cent.), and a large fraction showing definite conjugated carbonyl absorption (λ_{max} $227\text{ m}\mu$; infra-red bands at 1690 and 1637 cm^{-1}) and also carbonyl absorption in the region of 1715 – 1720 cm^{-1} (a broadened indefinite band), but no alcohol absorption bands. Attempts to distil anything from the latter fraction were unsuccessful. These results are substantially in agreement with those reported by Horn and Matic (*loc. cit.*), but it has been found that the products obtained under normal saponification conditions are largely artefacts, and an explanation of their formation is proposed.

Although such a large portion of the products from heating the cuticle wax with alkali cannot be distilled, it has now been found that most of the wax itself distils at a relatively low temperature. At 0.5 mm pressure approximately 90 per cent. of the wax distils at 220 – 235°C as a colourless oil, which rapidly sets to a crystalline wax. The distilled wax then has an infra-red band at 1725 cm^{-1} in Nujol, and at 1733 cm^{-1} , with a shoulder at 1713 cm^{-1} , in carbon tetrachloride solution, and is readily converted into a series of carbonyl derivatives in yields of about 50 per cent. of the calculated amounts, assuming an average chain-length of C_{28} as indicated by the analytical results. It forms crystalline 2,4-dinitrophenylhydrazones (m.p. 100 – 102°C); crystalline semicarbazones (m.p. 112 – 114°C); and oximes (m.p. 88 – 90°C) which have an infra-red spectrum closely similar to that of heptadecanaldoxime. The remainder of the distillate is composed of long-chain alcohols, isolated as colourless crystals (m.p. 80 – 82°C) in approximately 30 per cent. yield, long-chain acids (*c.* 10 per cent.) and hydrocarbons (*c.* 6 per cent.). The presence of alcohols accounts for the band at 3685 cm^{-1} in the infra-red spectrum of the distillate, and the acids may account for the shoulder on the aldehyde band when the spectrum is measured in carbon tetrachloride solution.

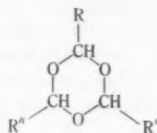
That aldehydes and not ketones are produced by distillation of the wax is shown by (i) the position of the carbonyl band in the infra-red spectrum of the distillate, (ii) dehydration by heating in acetic anhydride of the oximes prepared from the distillate to give nitriles, but no amides, (iii) the formation from the distillate of condensation products with dimedone and with 1,2-dianilinoethane, a reagent specific for aldehydes (Wanzlick and Löchel 1953).

The formation of aldehydes in such high yield by distillation of the wax might result from either a retroaldol reaction, or depolymerization of polymeric aldehydes. Since only aldehydes and no corresponding amount of ketones have been obtained, aldol compounds, if present, must be derived from two

molecules of aldehyde as in structure I, but the properties of the wax appear to be more satisfactorily explained by a polymeric aldehyde structure, probably of the trioxane type II. Such polymeric aldehydes are known to be resistant to oxidation by potassium permanganate in acetone, and to be easily depolymerized on heating (Le Sueur 1905). Since long-chain alcohols are also present, some at least of the aldehydes in both the cuticle wax and the distilled wax may occur as hemiacetals, for Zaar (1932) has claimed that aldehydes and alcohols of medium chain length form hemiacetals when heated in the absence of any catalyst. However, after heating dodecanal with more than one equivalent of dodecanol the mixture still showed aldehyde absorption at 1730 cm^{-1} .



(I)



(II)

The products formed by heating cuticle wax with ethanolic potassium hydroxide solution are readily explained when the presence of aldehydes is taken into account. Thus some acids and alcohols, previously assumed to be formed from esters, could well result from a Cannizzaro reaction, and the large non-distillable fraction showing carbonyl absorption could result from aldol condensation and subsequent dehydration. A product having similar spectroscopic properties to those of the unsaponifiable fraction of sugar-cane wax is obtained from partially polymerized dodecanal by heating it with ethanolic potassium hydroxide. In particular it has $\lambda_{\text{max.}} 227\text{ m}\mu$, conjugated carbonyl bands in the infra-red spectrum at $1696, 1645\text{ cm}^{-1}$, and some absorption in the unconjugated carbonyl region at $c. 1725\text{ cm}^{-1}$ (as a liquid film). The residue remaining in the flask when the wax is distilled also had $\lambda_{\text{max.}} 227\text{ m}\mu$ showing that it contains some of the dehydrated aldol compound. This may indicate that some of the aldol compound does occur in the wax, but condensation of the aldehydes with elimination of water probably occurs during distillation.

Not only the saponification value of the wax, but also its hydroxyl value and iodine value may be explained by the presence of aldehydes. Under the conditions used for measuring the hydroxyl value some formation of enolic acetates from aldehydes could be expected, and control experiments with heptaldehyde show that it also appears to have a high iodine value.

The change of sugar-cane cuticle wax into free aldehydes takes place very readily. After dissolving in carbon tetrachloride by warming, the solution shows a strong band at 1733 cm^{-1} , and measurements on a Nujol mull show a noticeable change in the absorption of the wax after keeping at 60°C under nitrogen for only 5 min. Moreover wax which has been dissolved in hot ethanol gives 2,4-dinitrophenylhydrazones, although not in such high yield ($c. 20\text{ per cent.}$ only) as the freshly distilled wax. Presumably considerable formation of free

aldehyde takes place during the isolation of the cuticle wax by extraction with hot light petroleum.

Cuticle wax is rapidly oxidized if melted when exposed to the air. Thus melted wax kept at 110 °C in air for 4 hr showed an increase in acid value from 17 to 56, and a greatly increased infra-red absorption at 1715 cm^{-1} . When air is excluded this rapid oxidation does not occur, and the small amount of acids formed under these conditions is approximately equivalent to the amount of peroxides or hydroperoxides in the wax.

Sugar-cane cuticle wax is the first plant wax known to be a source of long-chain aldehydes, and it would be interesting to test other grass waxes for the presence of similar compounds. The occurrence of stearaldehyde in the volatile oil from *Cinnamomum nigranthum* Hayata has been reported by Ikeda (1930) and aldehydes of shorter chain length have been isolated from a large number of essential oils, for example, decanal and dodecanal from oils of *Abies alba*, sweet orange, rue, and Okinawa pine (numerous references cited by Guenther and Althausen 1949).

Sugar-cane wax then is composed of polymeric aldehydes, free alcohols and acids, and a small percentage of hydrocarbons. There is no reason to postulate the presence of esters. The unusual composition and properties of the cuticle wax emphasize the need for full chemical and spectroscopic examination of waxes and oils to determine the structure of their components. Without such information the routine measurement of saponification values, hydroxyl values, and iodine values can give very misleading results. The presence of material easily converted into free aldehydes in the original sugar-cane cuticle wax, and its consequent susceptibility to chemical change, explains the need experienced by manufacturers of refined wax to extract the crude wax from sugar-cane mud immediately after production if a uniform material is to be obtained.

III. EXPERIMENTAL

(a) General

Microanalyses were carried out in the C.S.I.R.O. and University of Melbourne Microanalytical Laboratory. Melting points are corrected. Ultraviolet absorption spectra of wax derivatives were determined in heptane solution. The alumina used for chromatography was Spence, type H, which was neutralized by washing with ethyl acetate, dried, and heated to give the required degree of activity. In the text light petroleum refers to a fraction of boiling range 60–80 °C.

(b) Properties of Sugar-Cane Cuticle Wax

Samples of sugar-cane wax were collected at four Sugar Experiment Stations (Gordonvale (North); Bundaberg (South); Ayr, and Mackay) by scraping unburnt stalks of sugar-cane (var. Pindar) with wire brushes. The scrapings collected at these stations, on extraction with hot light petroleum in a Soxhlet type apparatus having the thimble surrounded by hot vapour, yielded a total of approximately 500 g of very light coloured wax (Found, in a single specimen: C, 82.0; H, 12.7; O, 5.0%). The four specimens were examined separately to check the uniformity of the waxes: all had approximately the same melting point, over the range 74–78 °C, negligible ultraviolet absorption, and almost identical infra-red absorption spectra, showing bands in Nujol at 3400–3420 cm^{-1} (hydroxyl) and at 1715 cm^{-1} (carbonyl). For comparison, a sample of cetyl palmitate had a band at 1735 cm^{-1} in Nujol, and stearic acid at 1710 cm^{-1} . In carbon tetrachloride solution the wax had bands at 3687 cm^{-1} (sharp), 2732 cm^{-1} (sharp),

1733 cm^{-1} (very strong, sharp, with shoulder at 1713 cm^{-1}). The waxes all gave negative Liebermann-Burchard tests.

The following estimations were also made on the four waxes according to standard procedures, the results being tabulated below (Table 1):

(i) Acid values were estimated on 0.1 g samples, using a mixture of isopropanol, benzene, and water (50:49:1) as solvent, and titrating with 0.1N potassium hydroxide in isopropanol.

(ii) Saponification values were determined by the method of Findley and Brown (1953), by refluxing the wax (0.5 g) with toluene (5 ml) and 0.5N ethanolic potassium hydroxide (5 ml) for 2 hr. However, the reaction taking place under these conditions is not a saponification reaction but probably a Cannizzaro reaction, and the result should not be regarded as a true saponification value.

(iii) After heating with ethanolic potassium hydroxide, as in (ii), the acidic fractions and unsaponifiable fractions were separated according to the method of Horn and Matic (1957).

(iv) Hydroxyl values were determined by the method of Findley and Brown (1953). Some acetylation of aldehydes may be expected to take place under these conditions and the result should not be taken as a measure of the amount of alcohol only.

(v) Iodine values were determined by the Wijs method using a reaction time of 1 hr. In a control experiment heptaldehyde showed an iodine value of 114.8.

(vi) The peroxide value of one wax (Gordonvale) was estimated by the British Standard Method (1950) using an 0.002N sodium thiosulphate solution. A titre of 6 ml/l g of wax was obtained, indicating 0.6 mm of peroxide (or hydroperoxide)/100 g wax.

(c) *Heating Cuticle Wax with Ethanolic Potassium Hydroxide*

After heating the wax with ethanolic potassium hydroxide the products were separated into acids and unsaponifiables as in (b) (iii). For yields see Table 1.

TABLE I

Wax	Acid Value	Saponification Value	Yield* of Acids (%)	Yield* of Unsaponifiables (%)	Apparent Hydroxyl Value	Iodine Value
Gordonvale (North)	17.0	36.4	14.7	85.0	43.8	18.7
Bundaberg (South)	14.7	32.2	14.5	86.7	40.0	21.1
Ayr ..	15.3	31.0	13.6	84.3	43.0	29.6
Mackay	18.7	39.9	13.7	86.0	34.8	29.5

* Obtained by method of Horn and Matic, see Subsection (b) (iii).

(i) *Acids*.—The mixture of acids had a strong infra-red band at 1710 cm^{-1} (Nujol) and the spectrum closely resembled those of stearic acid and arachidic acid, showing the absence of hydroxy acids. The acids were converted into their ethyl esters, and the esters purified by passage through a short column of alumina. The purified ethyl esters had saponification value 126 (Calc. for ethyl ester of a C_{28} acid, 124), and the crystalline acids obtained by saponification had a melting point of 75–78 $^{\circ}\text{C}$.

(ii) *Unsaponifiables*.—Hydroxyl values determined on the unsaponifiables as in (b) (iv) gave Gordonvale, 59.2; Bundaberg, 48.7; Ayr, 58.1; Mackay, 46.3. The infra-red spectrum (Nujol) of the unsaponifiables had a strong, slightly asymmetric band at 3360 cm^{-1} (hydroxyl); weak broad carbonyl absorption at 1715–1730 cm^{-1} ; and sharp conjugated carbonyl bands at 1690 and 1637 cm^{-1} . The ultraviolet spectrum showed λ_{max} 227 μ ; $\epsilon_{1\%}^{1\text{cm}}$ 33. Chromato-

graphy on alumina, activity 2, gave a clear-cut separation into two fractions. The first, fraction A, eluted by a mixture of light petroleum and toluene, showed carbonyl and conjugated carbonyl absorptions (a broad ill-defined carbonyl band; sharp well-defined conjugated carbonyl (1690 cm^{-1}) and double bond conjugated with carbonyl at 1637 cm^{-1}), but no hydroxyl absorption. It had λ_{max} . $227\text{ m}\mu$; $E_{1\text{ cm}}^{1\%}$ 57. The second, fraction B, eluted by warm chloroform, showed strong hydroxyl absorption but no carbonyl absorption.

Attempts to distil fraction A at low pressure were unsuccessful. Reduction over platinum oxide in toluene was slow, but finally gave a product, m.p. $80-82^\circ\text{C}$, having no conjugated carbonyl absorption (only a broad band at 1720 cm^{-1} , with weak hydroxyl absorption at 3300 cm^{-1} ; no ultraviolet absorption). This reduced material was heated with hydroxylamine hydrochloride and pyridine and attempts made to rearrange the product of oximation.

In separate experiments it was heated with polyphosphoric acid, acetic acid-sulphuric acid, and with benzene sulphonyl chloride in pyridine, but in no instance did the infra-red spectrum of the crude product indicate that a Beckmann rearrangement had taken place. Model experiments carried out for comparison with stearone oxime showed that with any of these reagents almost quantitative conversion into the amide occurred. The product, octadecanoyl heptadecylamine, obtained from stearone oxime, had m.p. $97-98^\circ\text{C}$ and strong bands characteristic of amide in its infra-red spectrum at 3317 , 1636 , and 1565 cm^{-1} .

Fraction B amounted to approximately 40% of the unsaponifiables. It consisted of alcohols only and had a strong infra-red band at 3350 cm^{-1} (Nujol), which resembled that of cetyl alcohol.

(iii) *Hydrocarbons*.—In the course of separating fractions A and B of the unsaponifiable material a small hydrocarbon fraction was isolated from the portion most rapidly eluted. It was mixed with some material showing carbonyl absorption, and was purified by oximation and further chromatography. Light petroleum then eluted a fraction (c. 6% of the original wax) having only typical hydrocarbon infra-red absorption and m.p. $59-61^\circ\text{C}$.

(iv) *Heating Dodecanal with Ethanolic Potassium Hydroxide*.—Dodecanal polymer mixed with some free dodecanal (0.2 g) was dissolved in ethanolic potassium hydroxide (0.5N; 5 ml) and light petroleum (5 ml) and refluxed for 3 hr. The unsaponifiable fraction, after separating from the acids formed, was obtained in 81% yield as a colourless liquid, which had λ_{max} . $227\text{ m}\mu$, $E_{1\text{ cm}}^{1\%}$ 111 in hexane. As a liquid film it had infra-red bands at c. $3400-3420\text{ cm}^{-1}$ (broad); c. 1725 cm^{-1} (weak, broad); 1696 cm^{-1} (medium, sharp); and 1645 cm^{-1} (weak).

(d) *Distillation of Cuticle Wax*

A sample of cuticle wax (5.0 g) was distilled at 0.5 mm pressure and the fraction (4.6 g) boiling at $220-235^\circ\text{C}$ collected. In separate experiments it was found that approximately 50% of the wax distils steadily at $220-222^\circ\text{C}$ at 0.5 mm. The distillate, m.p. $74-78^\circ\text{C}$, had infra-red bands in Nujol at $3400-3500\text{ cm}^{-1}$ (broad, medium) and at 1725 cm^{-1} (strong band with broad base), and in carbon tetrachloride solution at 3685 cm^{-1} (medium, sharp), 2730 cm^{-1} (sharp), 1733 cm^{-1} (very strong, sharp, with slight shoulder at 1713 cm^{-1}); there was only general low absorption in the ultraviolet. The distilled wax was much more readily soluble in hot ethanol than the original wax. It had an acid value of 14 and after standing for 1 week the infra-red spectrum (Nujol) was substantially the same. The distilled wax was converted into the following derivatives:

(i) *2,4-Dinitrophenylhydrazones*.—The 2,4-dinitrophenylhydrazones were prepared by adding ethanolic 2,4-dinitrophenylhydrazine reagent to a solution of distilled wax (0.95 g) in hot ethanol (50 ml). The solution was boiled for 1 min and filtered. Yellow crystalline 2,4-dinitrophenylhydrazones separated on cooling, and were filtered from the slightly warmed solution. If allowed to stand at room temperature some gelatinous material separated and made filtration difficult unless the solution was warmed. After the initial filtration the 2,4-dinitrophenylhydrazones were easily crystallized from ethanol giving yellow prisms, m.p. $100-102^\circ\text{C}$, with previous sintering. The 2,4-dinitrophenylhydrazones had an ultraviolet absorption spectrum closely similar to that of nonanal-2,4-dinitrophenylhydrazone. A spectroscopic estimation was made of the amount of 2,4-dinitrophenylhydrazones in the crude product (1.08 g; 78%) first filtered off, by comparing the intensity of the absorption at $357\text{ m}\mu$ with the value obtained

with pure nonanal 2,4-dinitrophenylhydrazones. This showed that the 2,4-dinitrophenylhydrazones are actually formed in approximately 60% yield, assuming an average chain length of C_{28} (Found, on twice crystallized material: C, 70.8; H, 10.4; N, 8.9%. For comparison, the 2,4-dinitrophenylhydrazone of octacosanal has C, 69.4; H, 10.2; N, 9.5%).

(ii) *Semicarbazones*.—The semicarbazones were prepared by adding a semicarbazide solution (prepared by heating semicarbazide hydrochloride (1 g), sodium acetate (1 g) in ethanol (30 ml), and filtering) to a hot solution of distilled wax (3.85 g) in ethanol (150 ml). Crystalline semicarbazones separated on cooling and after allowing to stand for 30 min the solution was warmed slightly to dissolve some gelatinous material. Filtration then gave colourless prisms, m.p. 109–111 °C; yield, 2.75 g, which melted at 112–114 °C after recrystallization from ethanol (Found: C, 75.5; H, 12.8; N, 9.2%. For comparison, the semicarbazone of octacosanal has C, 74.8; H, 12.7; N, 9.0%).

(iii) *Oximes*.—The yield of oximes prepared directly from distilled wax (1.0 g) was lower (0.4–0.45 g), probably because of the greater solubility of oximes in warm ethanol. The oximes were obtained as colourless prisms, m.p. 88–90 °C, with some previous sintering (Found: C, 79.8; H, 13.5; N, 3.1%. For comparison, the oxime of octacosanal has C, 79.4; H, 13.5; N, 3.3%). The infra-red spectrum of the oximes was closely similar to that of heptadecanaldoxime, having bands at 3230 and 1673 cm^{-1} (Nujol), whereas stearone oxime has bands at 3180, 3240, and 1650 cm^{-1} .

When the oximes were heated in acetic anhydride solution and the solution evaporated under reduced pressure, the residue showed nitrile absorption, having a sharp well-defined band at 2262 cm^{-1} (cf. Kitson and Griffith 1952) and no bands characteristic of an amide. Distillation of the nitriles gave a colourless product, m.p. 66–67.5 °C, having an infra-red absorption similar to that of heptadecane nitrile (Found: C, 82.6; H, 13.4; N, 3.2%).

Hydrolysis of the nitriles by heating with aqueous alcoholic sodium hydroxide solution as described by Levene and Taylor (1924) gave acids mixed with some amide (infra-red bands at 3230, 3440, and 1650 cm^{-1} with a shoulder at 1630 cm^{-1} , m.p. 105–107 °C) from incomplete hydrolysis of the nitrile. Complete hydrolysis was obtained by heating the crude product with potassium hydroxide in *n*-amyl alcohol. The resulting acids melted at 82–84 °C after one crystallization from light petroleum, and had equivalent weight 430 (Calc. for a C_{28} acid, 424).

The total product obtained by oximation of the distilled wax was also heated with acetic anhydride without first attempting to separate the oxime from alcohol acetate. The resulting product showed nitrile and ester absorption but no amide bands.

(iv) *1,2-Dianilinoethane Derivatives*.—The reagent consisted of dianilinoethane (5.3 g) and acetic acid (50% aqueous; 1.2 ml) in ethanol (100 ml), instead of methanol as originally described by Wanzlick and Löchel (1953). On addition of some of this solution to a hot solution of the distilled wax (1.15 g) in ethanol (70 ml) turbidity rapidly developed. Crystallization occurred as the solution cooled, and the product was filtered from the warm solution. Yield, 1.0 g (59%). The product was much less soluble in hot ethanol than the distilled wax (Found: C, 83.9; H, 11.7; N, 4.5%. For comparison the octacosanal derivative would have C, 83.7; H, 11.6; N, 4.7%).

(v) *Dimedone Derivatives*.—An ethanolic solution of dimedone (1 g), containing a drop of piperidine, was added to a hot solution of distilled wax (1.3 g) in ethanol (50 ml). After heating on a steam-bath for 5 min the solution was allowed to cool and the crystalline product filtered, after warming gently to dissolve gelatinous material. After several crystallizations the dimedone derivative (0.6 g) was obtained as colourless prisms which melted over the range 77–80 °C with some previous shrinking (Found: C, 79.1; H, 11.9%).

(vi) *Non-Aldehydic Components of Distilled Wax*.—The non-aldehydic components of the distilled wax were separated as follows: the mother liquors from filtration of the semicarbazones (or 2,4-dinitrophenylhydrazones) were diluted with water and the material which separated was extracted by shaking with warm light petroleum. The solution in light petroleum was washed with hot dilute aqueous-alcoholic sodium hydroxide solution to remove acids, and then evaporated under reduced pressure. The residue was heated with acetic anhydride–pyridine and the recovered acetylated material was chromatographed on alumina, and finally saponified by heating in

ethanolic potassium hydroxide solution. After dilution with water and extraction with hot light petroleum, the alcohols, obtained in approximately 30% yield, were crystallized once from ethanol. This gave colourless plates, m.p. 80–82 °C, which showed infra-red absorption c. 3300 cm⁻¹ (in Nujol) and had a closely similar infra-red spectrum to that of cetyl alcohol (Found: C, 82.8; H, 14.4%. For comparison octacosanol has C, 82.0; H, 14.1%, and melts at 83.4–83.6 °C). The acetates prepared from these alcohols melted at 62–64 °C (Found: C, 79.9; H, 13.2; acetyl, 9.8%. For comparison the acetate of octacosanol has C, 79.6; H, 13.4; acetyl, 9.5%, and melts at 64.6–64.8 °C; Piper, Chibnall, and Williams 1934).

A sample of the residue remaining in the flask after distillation of most of the wax was dissolved in chloroform and passed through a short tube of alumina to remove dark coloured impurities. The light brown material eluted had infra-red bands at 1733 cm⁻¹ with a shoulder at 1720 cm⁻¹; 1690 cm⁻¹ (sharp) and slight hydroxyl absorption at 3400–3500 cm⁻¹. The ultraviolet spectrum showed λ_{max} 227 m μ , $E_{1\%}^{1\text{cm}}$ 37.

(e) Effect of Heating Cuticle Wax at Lower Temperatures

After heating the cuticle wax at 60 °C for 5 min under nitrogen there was a shift in the position of the carbonyl band to 1725 cm⁻¹; after heating at 100 °C for 5 min there was a slight further shift to 1727 cm⁻¹. Both samples showed strong hydroxyl absorption at c. 3400–3500 cm⁻¹.

Heating a sample of wax in an atmosphere of nitrogen at 100 °C for 1 hr produced a slight change in its acid value (from A.V. 14.6 to 15.7; approximately equivalent to the peroxide content of the wax).

Wax having an initial acid value of 17 was melted at 110 °C in an oven, exposed to the air but without stirring. The following changes in acid value were observed: after 1 hr, 35; 2 hr, 56; 6 hr, 57. There was a corresponding change in the infra-red absorption which showed much more intense absorption in the carbonyl region at 1715 cm⁻¹.

IV. ACKNOWLEDGMENTS

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THE DECOMPOSITION OF LASIOCARPIC AND ECHIMIDINIC ACIDS IN HYDROCHLORIC ACID

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Summary

In concentrated hydrochloric acid at 100 °C, lasiocarpic acid is readily decomposed with formation principally of acetaldehyde, dimethylpyruvic acid, and α -keto- β -dimethyl- γ -valerolactone. Echimidinic acid is similarly and more rapidly decomposed while trachelanthic and heliotric acids are stable at 100 °C. In dilute hydrochloric acid, lasiocarpic acid is slowly converted into acetaldehyde, acetone, dimethylpyruvic acid, (+)-2-methoxy-4-methylpentan-3-one (IX), 2-methylpent-1-en-3-one (XI), and an unidentified compound.

The isolation of IX shows that lasiocarpic and heliotric acids have the same absolute configuration at the asymmetric carbon atom which bears the methoxyl group.

I. INTRODUCTION

Lasiocarpic acid (I), macrotopic acid (II), and echimidinic acid (II)[†] differ from other similar acids which occur esterified in the pyrrolizidine alkaloids of the family Boraginaceae, in that they have a tertiary hydroxyl group in a β -position to the carboxyl. This tertiary hydroxyl is the feature which makes them, and particularly their esters, subject in sodium hydroxide solution to a retroaldol type reaction which results in formation of acetone and a hydroxy-methoxy- or dihydroxybutyric acid (Drummond 1951; Petrova, Denisova, and Menshikov 1957; Denisova, Petrova, and Menshikov 1958). Trachelanthic and viridifloric acids (III), which have a secondary β -hydroxyl group, are stable under the same conditions (Culvenor 1954; Culvenor and Crowley 1959).

In the course of an attempt to demethylate lasiocarpic acid it has been found that presence of the tertiary β -hydroxyl group also promotes instability of lasiocarpic acid towards strong acid. Under conditions which do not affect heliotric acid (IV) and trachelanthic acid, lasiocarpic acid is decomposed with rearrangement and fission of the carbon skeleton. This decomposition, mentioned in an earlier paper (Culvenor 1956), is now described.

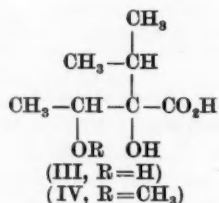
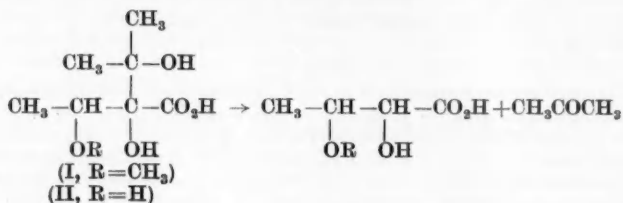
II. DECOMPOSITION IN CONCENTRATED HYDROCHLORIC ACID

In concentrated hydrochloric acid at 100 °C, the decomposition of lasiocarpic acid proceeded smoothly and without the resinification which occurred in refluxing hydrobromic acid. The major products were found to be acetaldehyde, dimethylpyruvic acid, and a neutral compound $C_7H_{10}O_3$. A compound $C_6H_{12}O_2$ (A) was isolated as its 2,4-dinitrophenylhydrazone in small amount. The

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[†] The name echimidinic acid is preferred for the acid structure II present in echimidine and heliosupine (Culvenor 1956) until it is known whether or not it is identical with macrotopic acid.

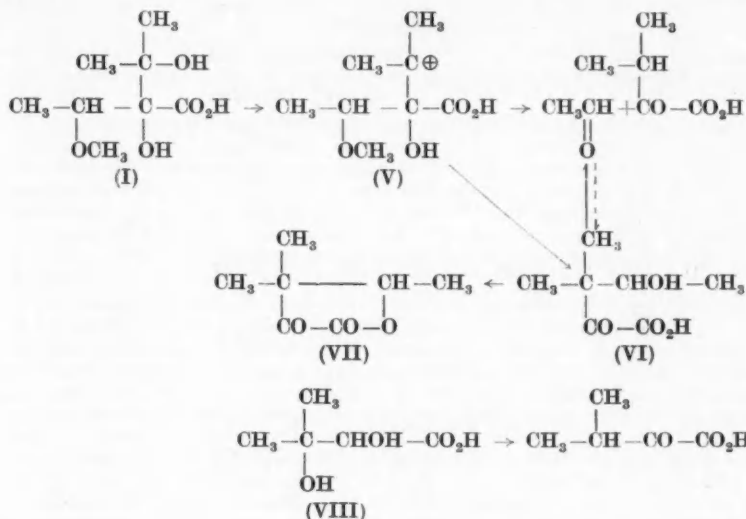
compound $C_7H_{10}O_3$ which formed a 2,4-dinitrophenylhydrazone and contained a five-membered lactone ring (infra-red absorption at 1784 cm^{-1} (Nujol), 1788 cm^{-1} (chloroform)), was found to be identical with α -keto- $\beta\beta$ -dimethyl- γ -valerolactone (VII) prepared by condensation of dimethylpyruvic acid with acetaldehyde in the presence of potassium carbonate. Similar condensation of dimethylpyruvic acid with formaldehyde to give α -keto- $\beta\beta$ -dimethyl- γ -butyrolactone has been described by Kuhn and Wieland (1942).



From the nature of the products it is clear that the initiating step in the breakdown of lasiocarpic acid is the loss of the β -OH group. With demethylation occurring at an unknown stage, the carbonium ion intermediate (V) may decompose to give dimethylpyruvic acid and acetaldehyde directly but to some extent at least it also undergoes a pinacol rearrangement to give VI which by lactonization yields the product VII. VI is an alternative source of the dimethylpyruvic acid and acetaldehyde since a similar acid-induced change, the loss of formaldehyde from methyl hederagonate, has been reported by Barton and de Mayo (1954). An asymmetric group, migrating in a pinacol rearrangement, does so with retention of configuration and the lactone (VII) as obtained from lasiocarpic acid might therefore be expected to be optically active. However, no optical activity could be detected and no change in melting point was observed when it was mixed with the inactive synthetic lactone.

A closely similar reaction, conversion of $\alpha\beta$ -dihydroxyisovaleric acid (VIII) into dimethylpyruvic acid by heating with mineral acid, has recently been described by Hall and Walmsley (1957). These authors consider the reaction simply as dehydration of a β -hydroxy acid but formal pinacol rearrangement with migration of a hydrogen atom is also possible. The conversion of VIII into dimethylpyruvic acid can be brought about enzymatically in *Neurospora crassa* (Myers and Adelberg 1954) and the changes just described for lasiocarpic acid might therefore be considered as metabolic possibilities in connection with studies of the hepatotoxic properties of lasiocarpine.

Echimidinic acid (II) undergoes the same rearrangement in concentrated hydrochloric acid. Acetaldehyde and dimethylpyruvic acid were identified as products but no attempt was made to isolate the lactone (VII). The change is more rapid than with lasiocarpic acid, being complete in 10 min at 100 °C. Any possibility of preparing echimidinic acid (or a diastereoisomer) by demethylation of lasiocarpic acid in this way is thus precluded. A paper chromatographic study of the reactions of lasiocarpic acid with dilute and concentrated acid, at room temperature and at 100 °C, gave no evidence of formation of echimidinic acid.

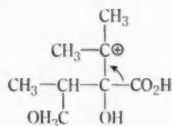


Trachelanthic acid (III) which has a secondary β -hydroxyl group and heliotric acid (IV) which has a methoxyl in the β -position were recovered unchanged after heating for several hours at 100 °C in concentrated hydrochloric acid. It is known that under more vigorous conditions, refluxing with concentrated hydrobromic acid, heliotric acid is demethylated to give trachelanthic acid (Adams and van Duuren 1953).

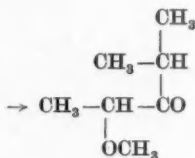
III. DECOMPOSITION OF LASIOCARPIC ACID IN DILUTE HYDROCHLORIC ACID

In 2N hydrochloric acid at 100 °C, lasiocarpic acid is only slowly decomposed, requiring more than 24 hr for complete reaction. Products were not obtained in good yield but the following were isolated (all as 2,4-dinitrophenylhydrazones): acetaldehyde, acetone, compound A ($\text{C}_6\text{H}_{12}\text{O}_2$), dimethylpyruvic acid, and compounds of empirical formulae $\text{C}_7\text{H}_{14}\text{O}_2$ (B) and $\text{C}_6\text{H}_{10}\text{O}$ (C). In one run, compound A was a major product but in a second run, it was not isolated at all. Compounds B and C were formed in only minor amounts. Compound B has been identified as (+)-2-methoxy-4-methylpentan-3-one (IX) by comparison with an authentic sample prepared by oxidation of heliotric acid with lead dioxide

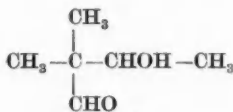
(Menshikov 1939), and evidently results from a third mode of decomposition of the initial intermediate V, namely decarboxylation. This may occur because of the decreased ease of demethylation and pinacol rearrangement in dilute acid solution. The isolation in this experiment also of acetaldehyde and dimethylpyruvic acid is evidence that these products are formed directly from V rather than from VI. The reaction of IX with dilute and with concentrated hydrochloric acid was examined to see whether compounds A and C were derived from this source. Compound C was formed but not A.



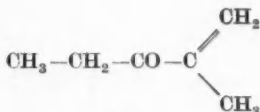
(V)



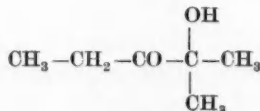
(IX)



(X)



(XI)



(XII)

Compound C forms an optically inactive 2,4-dinitrophenylhydrazone analysis of which indicates two *C*-methyl groups. The ultraviolet absorption spectrum of this 2,4-dinitrophenylhydrazone closely resembles the spectra reported for 2,4-dinitrophenylhydrazones of α -methylene ketones (Heilman, de Gaudemaris, and Arnaud 1952). It was identified as 2-methylpent-1-en-3-one by direct comparison of the semicarbazone and 2,4-dinitrophenylhydrazone with derivatives of authentic ketone prepared by the method of Colonge (1936). The 2,4-dinitrophenylhydrazone is described by Hart and Curtis (1957).

The structure of compound A is still uncertain. It forms an optically inactive 2,4-dinitrophenylhydrazone, the R_f value of which is in accord with the presence of a hydroxyl group, while analysis indicates 1.9 *C*-methyl groups. It is isomeric with X which could be formed by decarboxylation of VI. Preparation of X by condensation of isobutyraldehyde and acetaldehyde has been described by Drell and Dunn (1948) and by Kolobielski (1955) who reported a 2,4-dinitrophenylhydrazone (m.p. 122–123 °C) differing from that of compound A (146–147 °C). Repetition of this preparation gave an obvious mixture which, when chromatographed as dinitrophenylhydrazones, gave the compound of

Kolobielski but no trace of compound A. Another possible structure for compound A is 2-methylpentan-2-ol-3-one (XII) which could arise by decarboxylation. However, Aston and Greenburg (1940) report a melting point of 125–126 °C for the 2,4-dinitrophenylhydrazone of XII.

The isolation from lasiocarpic acid of IX in the same enantiomeric form as is obtained from degradation of heliotric acid, constitutes proof that these two acids have the same absolute configuration at the asymmetric carbon which bears the methoxyl group. The relative configuration of the two asymmetric centres in lasiocarpic acid is not yet known.

IV. EXPERIMENTAL

Microanalyses were carried out in the C.S.I.R.O. and Melbourne University Microanalytical Laboratory. Melting points are corrected. The abbreviation DNP means 2,4-dinitrophenylhydrazone.

(a) *Paper Chromatography*.—The solvents used for carboxylic acids were (i) the upper phase resulting from shaking butanol with an equal volume of 5% aqueous acetic acid, and (ii) a mixture of butanol and concentrated aqueous ammonia (30:1) saturated with water. Two different systems were employed for the dinitrophenylhydrazones. In the earlier stages they were chromatographed on paper impregnated with olive oil, with isopropanol–water (2:1) as the developing solvent (Seligman and Edmonds 1955). In the later stages, the system of Gasparic and Vecera (1957) with cyclohexane as developing solvent on a paper impregnated with dimethylformamide was employed. The second system is now preferred.

(b) *Reaction of Lasiocarpic Acid with Concentrated Hydrochloric Acid*.—(i) Lasiocarpic acid (0.5 g) and conc. HCl (10 ml) were heated at 100 °C for 2 hr with a slow stream of nitrogen bubbling through the solution and then passing into a solution of 2,4-dinitrophenylhydrazine hydrochloride. The latter yielded a precipitate (0.27 g), m.p. 130–135 °C, R_F 0.58 (acetaldehyde DNP has R_F 0.58). After completion of the reaction, the solution was distilled under reduced pressure into another solution of 2,4-dinitrophenylhydrazine hydrochloride. This gave a precipitate (0.33 g) which crystallized from benzene in long yellow needles, m.p. 198–199 °C (Found, on sample dried for 2 hr at 80 °C *in vacuo*: C, 48.8; H, 4.5; O, 29.4; N, 17.2; loss in weight at 120 °C, 7.7%. Calc. for $C_{15}H_{14}O_6N_4$: C, 48.4; H, 4.4; N, 17.4; loss in weight for $\frac{1}{2}(C_6H_6)$ removed, 8.1%. Found, on sample dried at 120 °C *in vacuo*: C, 44.7; H, 4.1; N, 18.4%. Calc. for $C_{11}H_{12}O_6N_4$: C, 44.6; H, 4.1; N, 18.9%). This DNP did not depress the melting point of that of authentic dimethylpyruvic acid, m.p. 200 °C (see below).

The crude DNP of m.p. 130–135 °C crystallized from methanol without improvement in melting point. When chromatographed on silica gel in benzene–light petroleum (50:50), a large fast-moving band and a small slow-moving band were formed. The former gave orange needles, m.p. 166–167 °C (from methanol), mixed m.p. 168–169 °C with authentic acetaldehyde DNP. The latter band, eluted with benzene, gave DNP of compound A which crystallized from a small amount of benzene in orange microneedles, m.p. 146–147 °C. It was not detected in other runs with conc. HCl.

(ii) Lasiocarpic acid (2 g) was refluxed in conc. HCl (30 ml) for 2 hr. The solution was cooled, diluted with water (60 ml), and extracted continuously with ether. The resulting oil (1.45 g) was distilled from a bulb tube, the main fraction (0.49 g) distilling at 60–70 °C/8 mm, leaving a residue (0.24 g). Redistillation of the distillate gave an oil, b.p. 66 °C/10 mm, R_F 0.65 in butanol–acetic acid, R_F 0.29 in butanol–ammonia. Although not pure (Found: C, 52.9; H, 7.9%. Calc. for $C_9H_8O_5$: C, 51.7; H, 6.9%), this oil is largely dimethylpyruvic acid since it readily formed a DNP, m.p. and mixed m.p. 199 °C, and reacted with *o*-phenylenediamine in dilute acetic acid to give 3-isopropyl-2-quinoxalinol, m.p. 233–234 °C, undepressed on admixture with an authentic sample (Section IV (f)).

When redistilled from a bulb tube, about one-half of the residue distilled at 80–90 °C/0.5 mm to give an oil which crystallized. Recrystallization from benzene–light petroleum and sublimation at 60 °C/1 mm gave prisms, m.p. 75–76 °C (Found: C, 59.2; H, 7.1; O, 33.6%. Calc.

for $C_7H_{10}O_3$: C, 59.1; H, 7.1; O, 33.8%). The compound is neutral, optically inactive, and melted undepressed on admixture with authentic α -keto- $\beta\beta$ -dimethyl- γ -valerolactone.

(c) *Attempted Detection of Echimidinic Acid.*—Solutions of lasiocarpic acid (3%) in conc. HCl and in dilute HCl (2N) were kept for 2 hr under two temperature conditions, 20 and 100 °C, and spotted at 15-min intervals on paper chromatograms. The papers were developed in butanol-acetic acid and printed (for detection of acids) with bromocresol green. In both reactions at room temperature lasiocarpic acid, R_F 0.73, remained unchanged. In conc. HCl at 100 °C, lasiocarpic acid had almost completely disappeared after 45 min with appearance of an acid of R_F 0.63 (dimethylpyruvic acid) but with no trace of echimidinic acid (R_F 0.55). In dilute HCl at 100 °C, lasiocarpic acid was largely unchanged after 2 hr, but a small amount of an acid, R_F 0.86, was formed.

(d) *Reaction of Echimidinic Acid with Conc. HCl.*—A test mixture of echimidinic acid in conc. HCl was kept at 100 °C and spotted on a paper chromatogram at 7-min intervals; nearly all the acid was decomposed in the first 7 min and no trace remained after 14 min. Echimidinic acid (0.25 g) heated in conc. HCl at 100 °C for 15 min and worked up as in Section IV (b) (i) gave acetaldehyde DNP, R_F 0.60, m.p. and mixed m.p. 166–167 °C, and dimethylpyruvic acid DNP, m.p. and mixed m.p. 199–200 °C.

(e) *Dimethylpyruvic Acid.*—An authentic sample was prepared from ethyl isopropylacetate by the method of Sen (1923). It had R_F 0.65 in butanol-acetic acid, R_F 0.28 in butanol-ammonia. It formed a DNP, m.p. 201 °C, which retained benzene of crystallization as described for the product from lasiocarpic acid (Section IV (b)).

(f) *3-isopropyl-2-quinazolinol.*—Dimethylpyruvic acid and *o*-phenylenediamine were mixed in dilute acetic acid to give a solid which crystallized from alcohol in needles, m.p. 234 °C (Found: C, 70.6; H, 6.5%. Calc. for $C_{11}H_{12}ON_2$: C, 70.2; H, 6.4%).

(g) *α -Keto- $\beta\beta$ -dimethyl- γ -valerolactone (VII).*—Dimethylpyruvic acid (1.2 g) was neutralized in water (6.7 ml) with solid K_2CO_3 . Acetaldehyde (0.45 g) was added and then solid K_2CO_3 (1.0 g) in small portions. After keeping overnight, water (5 ml) was added and the mixture acidified with 2N HCl while heating on a water-bath. Continuous extraction with ether gave an oil (1.6 g) which was distilled to give unchanged dimethylpyruvic acid (0.18 g), b.p. 65–70 °C/10 mm, DNP, m.p. 198–199 °C; an intermediate fraction (0.07 g); and the ketolactone (0.43 g), b.p. c. 70 °C/1.5 mm, forming prisms from benzene-light petroleum, m.p. 75–76 °C (Found: C, 59.2; H, 7.1%. Calc. for $C_7H_{10}O_3$: C, 59.1; H, 7.1%). In a capillary tube, the lactone boiled at about 235 °C at atmospheric pressure (cf. γ -valerolactone, b.p. 205–207 °C). The infra-red spectrum showed only one carbonyl band at 1784 cm^{-1} in Nujol, 1788 cm^{-1} in chloroform.

The ketolactone formed a DNP, orange needles from methanol, m.p. 209–210 °C (Found: C, 49.0; H, 4.7; N, 17.1%. Calc. for $C_{13}H_{14}O_5N_4$: C, 48.4; H, 4.4; N, 17.4%).

(h) *3-(1',1'-Dimethyl-2'-hydroxy)propyl-2-quinazolinol.*—The ketolactone (VII; 0.2 g) and *o*-phenylenediamine (0.2 g) were warmed to 60–70 °C in dilute acetic acid (10 ml), whereupon the lactone dissolved. A gum separated and after 1 hr, crystallized. Recrystallization from benzene or acetone gave needles, m.p. 177–178 °C (Found: C, 67.6; H, 6.8; N, 12.1%. Calc. for $C_{13}H_{16}O_2N_2$: C, 67.2; H, 6.9; N, 12.1%).

(i) *Reaction of Lasiocarpic Acid with Dilute HCl.*—(i) Lasiocarpic acid (1 g) was refluxed with 2N HCl (15 ml) for 20 hr in a stream of nitrogen which passed into a solution of 2,4-dinitrophenylhydrazine hydrochloride. From the latter was obtained a precipitate (0.34 g) R_F 0.40, 0.59, 0.81 in the cyclohexane-dimethylformamide system ("volatiles" DNP). The reaction solution was made alkaline with Na_2CO_3 and extracted with ether to give an oil (0.3 ml) which was distilled from a bulb tube at about 60–80 °C/70 mm. Conversion to the DNP gave a solid, m.p. 100–120 °C, R_F 0.15 (cyclohexane). Recrystallization from benzene-light petroleum gave the DNP of compound A, orange needles, m.p. 146–147 °C, undepressed on admixture with the DNP of similar m.p. reported in Section IV (b) (Found: C, 48.8; H, 5.5; N, 19.0; (C)Me, 9.6%. Calc. for $C_{12}H_{14}O_2N_4$: C, 48.6; H, 5.4; N, 18.9; 2(C)Me, 10.2%).

The residual reaction solution, acidified and extracted with chloroform, gave only a few mg of gum which was discarded. The "volatiles" DNP was chromatographed on cellulose powder

impregnated with dimethylformamide in cyclohexane saturated with dimethylformamide. Three bands formed and were eluted separately. The second gave material of R_F 0.57 in the cyclohexane system; recrystallized, this gave acetone DNP, m.p. and mixed m.p. 126–127°C. The last eluted gave material of R_F 0.42 in the cyclohexane system and on recrystallization yielded acetaldehyde DNP, m.p. and mixed m.p. 165–166°C. The band first eluted gave a solid R_F 0.80 (cyclohexane), which crystallized from light petroleum as mixed yellow needles and red prisms. These were separated mechanically, assisted by the fact that one usually crystallized out first. The yellow needles were recrystallized to give the DNP of compound B, m.p. 123–124°C (Found: C, 50.4; H, 5.9; N, 17.9; (C)Me, 8.7; OMe, 9.3%. Calc. for $C_{12}H_{18}O_4N_4$: C, 50.3; H, 5.8; N, 18.1; $2 \times$ (C)Me, 9.7; $1 \times$ OMe, 10.0%). It did not depress the melting point of the DNP of authentic (+)-2-methoxy-4-methylpentan-3-one (Section IV (j)) and had $[\alpha]_D^{20} + 234^\circ$ (c, 0.3 in ethanol). After recrystallization the red prisms, DNP of compound C, had m.p. 149–150°C (Found: C, 52.0; H, 5.2; N, 20.1%. Calc. for $C_{12}H_{14}O_4N_4$: C, 51.8; H, 5.0; N, 20.1%). From alcohol, it crystallizes in plates. When run on the same sheet of paper, in the cyclohexane system, this DNP and that of compound A had R_F values 0.78 and 0.19 respectively. The ultra-violet absorption spectrum shows λ_{max} at 364 m μ , ϵ_{max} 22500; cf. λ_{max} 369 m μ , ϵ_{max} 25000 for DNP of 3-ethylbut-3-en-2-one (Heilman, deGaudemaris, and Arnaud 1952).

(ii) Lasiocarpic acid (1.5 g) and 2N HCl (25 ml) were refluxed for 20 hr and the solution cooled and poured into a solution of 2,4-dinitrophenylhydrazine hydrochloride. An initial precipitate (yellow, 0.12 g) had R_F 0.00 in the cyclohexane system and crystallized from benzene in fine yellow needles, m.p. 199–200°C, mixed m.p. 200–201°C with the DNP of dimethylpyruvic acid. A subsequent precipitate (0.15 g, reddish colour) had R_F 0.00, 0.79. It was extracted with light petroleum and the extract concentrated and crystallized from ethanol to give the DNP of compound C, m.p. 148–149°C, R_F 0.79.

(j) (+)-2-Methoxy-4-methylpentan-3-one (IX).—The ketone (IX) was prepared by oxidation of heliotric acid with lead oxide by the procedure of Menshikov (1939). The volatile product boiled entirely at 140–142°C. The 2,4-dinitrophenylhydrazone crystallized from light petroleum in yellow needles, m.p. 123–124°C, $[\alpha]_D^{20} + 236^\circ$ (c, 0.30 in ethanol) (Found: C, 50.4; H, 5.7; N, 17.8%. Calc. for $C_{12}H_{18}O_4N_4$: C, 50.3; H, 5.8; N, 18.1%).

(k) Reaction of IX with HCl.—(+)-2-Methoxy-4-methylpentan-3-one (5 g) refluxed in conc. HCl for 4 hr gave an oil which was separated, washed with a small volume of Na_2CO_3 solution, and dried. On distillation the main fraction boiled between 134–140°C, $[\alpha]_D$ zero in ethanol. It formed a DNP in low yield, glistening red plates, m.p. and mixed m.p. with the derivative of compound C, 149°C; and with difficulty a semicarbazone, also in low yield, glistening plates, m.p. 156°C (Found: C, 54.1; H, 8.4%. Calc. for $C_7H_{12}N_2O_3$: C, 54.2; H, 8.4%). The semicarbazone, on solution in ethanol and addition of 2,4-dinitrophenylhydrazine in HCl gave the DNP, m.p. 149°C. The infra-red spectrum indicated that the ketone, b.p. 134–140°C, was a mixture of a hydroxyketone with a lesser amount of an $\alpha\beta$ -unsaturated ketone. No derivatives of the former could be prepared and no trace of the DNP of compound A was found.

When IX was refluxed with 2N HCl for 21 hr, very little dinitrophenylhydrazone was obtained from the resulting solution. Chromatographed on silica gel, it yielded the DNP of compound C, m.p. 148–149°C, and another component of R_F similar to that from the conc. HCl reaction.

(l) 2-Methylpent-1-en-3-one (XI).—1-Chloro-2-methylpentan-3-one, prepared by condensation of diethylketone with formaldehyde in the presence of dry HCl by the method of Colonge (1936) was distilled with dimethylaniline yielding the unsaturated ketone XI. This readily formed a DNP, glistening red plates, m.p. and mixed m.p. with that of compound C, 149°C (Found: C, 51.7; H, 5.1; N, 19.8%. Calc. for $C_{12}H_{18}O_4N_4$: C, 51.8; H, 5.0; N, 20.1%). The semicarbazone formed with ease and crystallized from aqueous ethanol as glistening plates, m.p. and mixed m.p. with semicarbazone described in Section IV (k), 158°C.

(m) Condensation of Acetaldehyde and isoButyraldehyde.—The procedure of Drell and Dunn (1948) was followed. Distillation of the product gave in about equal amounts, oils of b.p. 72–75°C/10 mm and b.p. 80°C/2 mm. The former yielded a mixed DNP, R_F 0.73 (main spot), 0.56, 0.36 (olive oil system), m.p. 110–115°C, after crystallization from benzene. The second fraction gave a DNP of similar R_F values, forming yellow needles, m.p. 164–167°C, from methanol.

In this system the DNP of compound A had R_F 0.73, that of isobutyraldehyde, R_F 0.34. Recrystallization of the DNP of the second fraction gave isobutyraldehyde DNP, m.p. and mixed m.p. 180–181 °C. Chromatography of the DNP of the first fraction on cellulose impregnated with olive oil, with isopropanol water (2 : 1) as eluant, gave the DNP of R_F 0.73 as orange needles, m.p. 110–115 °C, raised by recrystallization to 120–125 °C. The original mixed DNP was chromatographed again on cellulose-dimethylformamide in cyclohexane; this method gave orange needles, R_F 0.14, m.p. 129–130 °C, from benzene, apparently the DNP of X, in substantial amount. No fraction yielded material similar in melting point to the DNP of compound A.

V. ACKNOWLEDGMENTS

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CHEMISTRY OF AUSTRALIAN LICHENS

I. SOME CONSTITUENTS OF *PARMELIA CONSPERSA* (EHRH.) ACH., *RAMALINA FRAXINEA* (L.) ACH., *USNEA BARBATA* (L.) WIGG., AND *U. CERATINA* ACH.,
FROM THE NEW ENGLAND REGION

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Summary

Each of the species named in the title has yielded (+)-usnic acid, as found in previous investigations in other parts of the world. Other aromatic constituents isolated, except salazinic acid from *Parmelia conspersa*, differ from those previously reported and include a new compound from *P. conspersa*. It is suggested that usnic acid, previously obtained from *Usnea* spp. but unidentified, was a mixture of salazinic and norstictic acids.

D-Mannitol or D-arabitol has been isolated from the water-soluble fractions.

I. INTRODUCTION

Chemical constituents of European and Asian lichens have been widely studied, and the results of structural investigations have been summarized by Asahina and Shibata (1954). There appears to be no published investigation of the constituents of Australian lichens and we now report results for some lichens from the New England region of New South Wales.

Initial selection of species for examination was governed by availability of botanically homogeneous samples, these comprising *Parmelia conspersa* (Ehrh.) Ach., *Ramalina fraxinea* (L.) Ach., *Usnea barbata* (L.) Wigg., and *U. ceratina* Ach. The method of extraction adopted was successive exhaustion by cold percolation with each of a graded series of solvents. Concentration or evaporation of the extracts followed by selective extraction and fractional crystallization gave the aromatic compounds shown with yields in parentheses in Table 1. Quantitative separation is not to be expected and the yields quoted represent only lower limits to the amounts present, especially for norstictic acid in view of the wasteful procedure by which small amounts of the compound were obtained from mixtures containing it. Named compounds have the structures shown and were identified by analyses and/or properties of the compounds themselves and their characteristic derivatives. Compound P does not correspond to any in the literature: it is colourless, optically inactive, and has the probable molecular formula, $C_{22}H_{24}O_6$, containing two terminal methyl groups but no methoxyl group. A free carboxyl group is apparently not present but the compound is phenolic and forms a diacetyl

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derivative. It is distinguished from the majority of known colourless aromatic lichen compounds by its unusually low oxygen content (only rarely does the ratio of carbon to oxygen atoms rise above 3) and by its failure to give a colour with ferric chloride in ethanol; its solution in chloroform however gives a blue colour with the ferric chloride reagent of Soloway and Wilen (1952).

Table 1 also shows with leading references aromatic compounds of known structure (Asahina and Shibata 1954) isolated from lichens described by the same specific names in other parts of the world. The results for *U. barbata* include those for a number of subspecies and geographical variations in the constituents

TABLE 1

AROMATIC COMPOUNDS ISOLATED FROM CERTAIN LICHENS

Yields in parentheses are those obtained in the present work; alternative names in parentheses are those used in the publications cited

<i>Parmelia conspersa</i>	(+)-Usnic acid (0.50%) ^(a, b, c) ; salazinic acid (0.64%) ^(a, b) ; compound P, m.p. 188 °C (2.2%); acid of m.p. 205 °C; ^(a) lobaric acid; ^(b) stictic acid ^(c)
<i>Ramalina fraxinea</i>	(+)-Usnic acid (0.19%); (?) -usnic acid ^(d, e)
<i>Usnea barbata</i>	(+)-Usnic acid (1.8%) ^(d, e, f, g, h, i) ; norstictic acid (0.04%); salazinic acid (1.3%); barbatic acid ^(f, g, h) ; lobaric (usnetic) acid ^(g) ; atranorin (usnarin) ^(g) ; barbatolic (alectoric) acid ^(g, i) ; thamnolic (hirtellic) acid ⁽ⁱ⁾
<i>Usnea ceratina</i>	(+)-Usnic acid (0.73%) ^(g, h) ; norstictic acid (0.04%); salazinic acid (2.4%); barbatic acid ^(g, h) ; variolaric (parellic) acid ^(g)

^(a) Asahina and Asano (1933); ^(b) Zopf (1897, 1905); ^(c) Mohan, Keane, and Nolan (1937);

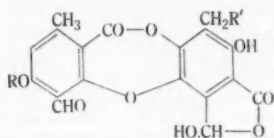
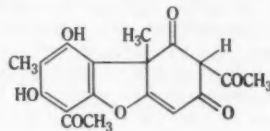
^(d) Rochleder and Heldt (1843); ^(e) Hesse (1861); ^(f) Stenhouse and Groves (1880); ^(g) Hesse (1903)—and references therein; ^(h) Zopf (1902); ⁽ⁱ⁾ Schöpfung and Heuck (1927); Schöpfung, Heuck, and Duntze (1931).

* But see du Vigneaud (1947) and Zopf (1902).

of these and of *U. ceratina* are discussed in detail by Hesse (1903). Variations in the compounds isolated from *P. conspersa* may be due solely to varietal differences but only one assignment, that of *P. conspersa* var. *hypoclysta* from Japan (Asahina and Asano 1933), was available for the results in Table 1.

The *Usnea* spp. have been reported (Hesse 1903 and references therein; Zopf 1902) to contain a substance, usnaric acid, of unknown structure, supposed by du Vigneaud (1945) to be salazinic acid. The reported properties and analysis (C, 57.5; H, 3.7%; no methoxyl) of usnaric acid are however better accounted for by the suggestion that it was a difficultly separable mixture of salazinic and norstictic acids similar to that encountered in the New England samples. In this connection it is interesting that Rangaswami and Rao (1955) have recently obtained salazinic and stictic acids from a sample of *U. florida*. Stictic acid contains a methoxyl group however and so cannot have been present in Hesse's usnaric acid.

Evaporation of the methanol extracts from the New England samples gave syrups completely soluble in water and showing three discrete spots on paper chromatograms with ammoniacal silver nitrate spray. The syrups presumably contained mixtures of polyols and carbohydrates, but only one component of each has so far been obtained crystalline. That from *P. conspersa* was D-mannitol, whereas that from each of the other species was D-arabitol. Lindberg, Misiorny, and Wachtmeister (1953) have isolated D-arabitol from, and obtained paper chromatographic evidence for D-mannitol in *P. conspersa* from Sweden, but water-soluble constituents of the other species have not been reported.

Salazinic acid ($R=H$; $R'=OH$)Norstictic acid ($R=R'=H$)Stictic acid ($R=Me$; $R'=H$)

Usnic acid

It has been suggested (Zopf 1902; du Vigneaud 1947) that extraneous compounds have sometimes been isolated as a result of contamination by foreign species. In the present work we believe that any contaminated samples were detected and rejected before chemical investigation. In particular, we suggest that compound P, the compound obtained in highest yield from *P. conspersa*, is unlikely to have been obtained from a minor (and therefore possibly undetected) contaminant.

II. EXPERIMENTAL

All melting points (except that of penta-acetylnorstictic acid, q.v.) were measured on a hot-stage under the microscope. The light petroleum used had b.p. 65–80 °C. Except where noted, samples for analysis were dried in a vacuum (0.1–0.01 mm) at 80–100 °C for several hours. Microanalyses are by the C.S.I.R.O. Microanalytical Laboratory under the direction of Dr. K. W. Zimmermann. The spectrum of usnic acid was measured in 95% ethanol in a Beckmann DU spectrophotometer.

(a) Extraction of the Lichens

Air-dried lichen collected by the authors was carefully hand-sorted from leaves, twigs, or pieces of stone, and shaken as free as possible of adhering soil. Representative samples were then submitted for competent botanical identification (to the late Mr. P. Bibby, National Herbarium, Melbourne). Occasionally contamination was at this point suggested, and the material collected was then rejected. Each identified botanically homogeneous sample was milled, placed in a glass column (3–7 cm dia.), and exhaustively percolated successively with cold light petroleum, ether, acetone, and methanol or 70% aqueous methanol, in this order. The light petroleum extracts were evaporated to small bulk on the water-bath and allowed to cool. The yellow solid was filtered off and washed with a little fresh solvent; in each case it proved to be (+)-usnic acid (see below). Evaporation of the filtrates gave greasy solids that were not further examined. No clear fractionation resulted from stepwise concentration of the ether or acetone extracts which were therefore usually evaporated to dryness from the water-bath. The methanol or aqueous methanol extracts were evaporated under reduced pressure from a water-bath

at less than 40 °C to syrups or aqueous liquors. Further treatment of each extract is described below.

Extraction of each sample occupied several weeks and extractions on more than one lichen species were carried on concurrently. The same compounds were isolated from more than one species, and identification of each known compound is described fully only for the extract from which the compound was first obtained pure. This sample of compound and any derivatives prepared from it are then described as "reference material". In each case properties given below agree closely with those in the original literature and cited by Asahina and Shibata (1954).

(b) Paper Chromatography of Depsidone Components

In the present work paper chromatography has been used principally for the detection and separation of salazinic and norstictic acids. Unbuffered Whatman No. 1 or No. 4 paper with *n*-butanol saturated with concentrated aqueous ammonia or *n*-butanol-acetone-water (5:1:2) (cf. Mitsuno 1953, who however used Toyo No. 50 paper) as developing medium led to much tailing, not observed with *n*-butanol-pyridine-water (3:1:1) as developing medium. A rapid and satisfactory combination was found in the use of buffered paper prepared by soaking Whatman No. 4 paper in 0.1M disodium hydrogen phosphate solution (pH 9), pressing it between thick sheets of filter paper, and drying it in air (Wachtmeister 1952) with *n*-butanol-acetone-water (5:1:2) as developing medium in the ascending method. The solvent front ascended 5-6 in. during 2 hr and clear separation occurred, salazinic acid having R_F 0.43 and norstictic acid R_F 0.52. The composition of the residual solvent (and with it R_F values) changed when the tank was opened at the beginning and end of runs presumably by preferential evaporation of acetone. This was of no moment as reference samples were always run on the chromatograms and one stock of solvent served several runs. The spots could be detected by spraying the chromatograms with bisdiazotized benzidine solution (red spots) or, more conveniently, freshly prepared 1% ethanolic *p*-phenylenediamine solution (clear yellow spots); ethanolic ferric chloride was unsatisfactory on the buffered papers.

(c) Paper Chromatography of Water-Soluble Constituents

Whatman No. 1 paper was used in the ascending method with *n*-butanol-pyridine-water (3:1:1) (Hough, Jones, and Wadman 1950) as developing medium. Spots, detected with the silver reagent of Partridge (1946), appeared at R_F values of 0.26, 0.20, and 0.06 in each case; only a spot at R_F 0.20 appeared with aniline hydrogen phthalate (Partridge 1949). Under our conditions *D*-arabitol had R_F 0.26 and *D*-mannitol and *D*-glucose R_F 0.20, only the last being detected with aniline hydrogen phthalate.

(i) *Parmelia conspersa* (Ehrh.) Ach.—(1) *Light Petroleum Extract*. The first runnings (2 l.) from one sample (920 g) evaporated to small bulk (100 ml) and cooled, deposited a mixture of long yellow needles and colourless silky needles. The latter were hand-picked as completely as possible and separated from adhering yellow crystals by suspension in cold light petroleum and decantation, the yellow material remaining behind. Two recrystallizations from light petroleum gave colourless prisms, m.p. 141 °C, but the yield was very low (c. 5 mg, 0.0005%) and the material was not observed on repetition of the extraction on another sample of lichen.

(+)-*Usnic Acid*: The bulk of the light petroleum extract together with the above yellow product gave golden yellow needles, m.p. 197-199 °C (3.1 g, 0.34%). Two recrystallizations from chloroform-ethanol gave (+)-usnic acid, m.p. 204-205 °C, $[\alpha]_D^{21} +501^\circ$ (c, 0.79 in CHCl_3). Light absorption: λ_{max} , 233, 282 m μ , $\log \epsilon_{\text{max}}$, 4.53, 4.40, resp.; λ_{min} , 254 m μ , $\log \epsilon_{\text{min}}$, 4.12 (cf. Barton, Deforin, and Edwards 1956) (Found: C, 62.6; H, 4.7%. Calc. for $\text{C}_{18}\text{H}_{16}\text{O}_7$: C, 62.8; H, 4.7%). The product gave a yellow solution in cold 2*N* sodium hydroxide, a red colour with ferric chloride in ethanol and, on being heated briefly with a solution of *p*-dimethylaminobenzaldehyde in 50% sulphuric acid, a reddish brown solution which, cooled and diluted with ethanol, became deep blue. In agreement with Foster, Robertson, and Healy (1939) no colour was produced when concentrated hydrochloric acid was used instead of 50% sulphuric acid.

(+)-*Diacetylusnic Acid*: Acetylation of (+)-usnic acid with acetic anhydride and pyridine gave a low yield of (+)-diacetylusnic acid, creamy-yellow needles, m.p. 199-200 °C, after several recrystallizations from methanol (cf. Schöpf and Heuck 1927).

(2) *Ether Extract.* Evaporation gave a yellowish residue which was refluxed with three portions (200 ml) of benzene for 30 min each time. Cooling the combined benzene extracts gave a colourless product (1.8 g, 0.20%) forming silky needles, m.p. 186–187 °C, from aqueous ethanol. Concentration of the benzene filtrate gave (+)-usnic acid (1.5 g, 0.16%), m.p. 202 °C, undepressed in admixture with reference material.

Compound P: The colourless residue (18.4 g, 2.0%) from the above benzene extraction formed long silky needles, m.p. 186–187 °C, from aqueous ethanol, undepressed in admixture with the colourless product from the benzene extracts. Recrystallization from ether–light petroleum gave small glistening flakes, m.p. 188–190 °C, or from aqueous ethanol or benzene needles, m.p. 188 °C, $[\alpha]_D^{20}$ 0.0° (c, 1.11 in EtOH) (Found: C, 69.2, 69.4; H, 6.6, 6.6; OCH₃, <0.5; C-CH₃, 6.4%. Calc. for C₂₃H₂₆O₈: C, 69.3; H, 6.6; 2 × C-CH₃, 7.5%). The compound dissolved readily in ether, acetone, chloroform, or ethanol, sparingly in light petroleum or cold benzene. It was insoluble in water or cold sodium carbonate solution, but dissolved instantly in cold, very dilute sodium hydroxide solution, and was recovered (m.p. alone or mixed with starting material, 186–187 °C) on acidification (hydrochloric acid or carbon dioxide). It gave no colour with ferric chloride in ethanol, but its solution in chloroform gave a blue colour with a solution of ferric chloride in chloroform and pyridine (Soloway and Wilen 1952).

Acetyl Derivative of Compound P: A solution of compound P (200 mg) in acetic anhydride (10 ml) and conc. sulphuric acid (2 drops) was kept at room temperature for 2 days, then poured onto ice. The oily product solidified and, after three recrystallizations from ether–light petroleum, formed clusters of needles, m.p. 104–105 °C (Found: C, 67.3; H, 6.3; COCH₃,* 18–19%. Calc. for C₂₇H₃₀O₈: C, 67.2; H, 6.3; 2 × COCH₃, 17.8%).

(3) *Acetone Extract.* Evaporation gave a yellowish solid. The colour was removed by extraction with a little boiling benzene.

Salazinic Acid: The residue (5.9 g, 0.64%) gave a single spot, R_f 0.43, on a paper chromatogram and was recrystallized from boiling 80% aqueous acetone to give salazinic acid monohydrate as fine needles, m.p. 260 °C (decomp.), after being dried in a vacuum desiccator over potassium hydroxide pellets and conc. sulphuric acid (Found (loss in a vacuum at 120 °C): H₂O, 4.4%. Calc. for C₁₅H₁₂O₁₀·H₂O: H₂O, 4.4%. Found in anhydrous material: C, 55.6; H, 3.6; C-CH₃, 4.0%. Calc. for C₁₅H₁₂O₁₀: C, 55.7; H, 3.1; C-CH₃, 3.9%). Anhydrous material had m.p. 260 °C (decomp.) after browning from 240 °C. It was sparingly soluble in water and common organic solvents including dry acetone but dissolved readily in hot 80% aqueous acetone. It gave a colourless solution in sodium hydrogen carbonate solution and, with cold 2N sodium hydroxide, a yellow solution which became reddish brown on heating. It gave a deep yellow colour with *p*-phenylenediamine and a reddish violet colour with ferric chloride in ethanol.

The above product was converted into the dianil, yellow prisms charring at 280 °C, and into hexa-acetylsalazinic acid, m.p. 176 °C, from aqueous acetone (Found: C, 54.5; H, 4.2; COCH₃,† 41.3%. Calc. for C₂₆H₂₄O₁₇: C, 54.7; H, 4.0; 6 × COCH₃, 39.2%).

Refluxing salazinic acid with acetic anhydride for 30 min in the absence of a catalyst gave on one occasion a product which was purified by chromatography from benzene on neutral alumina and then formed colourless prisms, m.p. 205–206 °C, from benzene. The product may have been triacetylsalazinic acid, but we have been unable to reproduce the result.

(4) *Aqueous Methanol Extract.* Evaporation of the methanol left an aqueous liquor (600 ml) which was filtered with the aid of kieselguhr and further clarified by treatment with 5% neutral lead acetate solution (100 ml) and filtration. Lead ions were removed from the filtrate with hydrogen sulphide, and the filtrate was concentrated under reduced pressure from a water-bath at 40 °C to a reddish syrup (32 g).

* The analyst reported that the acetic acid distillate was pink and determination of the end-point to phenolphthalein was difficult.

† Asahina and Asano (1933) also found that hexa-acetylsalazinic acid gave a high acetyl value but that salazinic acid itself gave an apparent acetyl value corresponding to the excess over the theoretical value.

D-Mannitol: A solution of the syrup in water (10 ml) was treated with ethanol (70 ml) whereupon a heavy gum was thrown down. After an hour the clear liquor was decanted; it slowly deposited a fawn solid (1.1 g) which was recrystallized from water (4 ml) and ethanol (20 ml) several times (once with charcoal) to give D-mannitol (450 mg) as colourless needles, m.p. 166 °C, undepressed in admixture with an authentic specimen. The product had $[\alpha]_D^{20} +13^\circ$ (c, 0.40 in 5% ammonium molybdate solution), and $[\alpha]_D^{18} +140^\circ$ (c, 0.40 in acidified ammonium molybdate solution). Richtmeyer and Hudson (1951) report $+16^\circ$ and $+141^\circ$ for these values, respectively.

The gum above thrown down by ethanol was retreated with water (10 ml) and ethanol (70 ml) and the clear liquor gave a further quantity (300 mg) of D-mannitol, m.p. 166 °C, undepressed in admixture with an authentic specimen, after several recrystallizations from water and ethanol.

The above product was converted into hexa-acetyl-D-mannitol, m.p. 123 °C, from ethanol, undepressed in admixture with an authentic specimen.

(ii) *Ramalina fraxinea* (L.) Ach.—(1) *Light Petroleum Extract.* Milled lichen (427 g) yielded (+)-usnic acid (0.8 g, 0.19%), $[\alpha]_D^{20} +503^\circ$ (c, 0.71 in CHCl_3), m.p. 202–203 °C, undepressed in admixture with reference material.

(2) *Ether Extract:* A negligible amount of intractable material was obtained.

(3) *Methanol Extract:* Treatment with charcoal and evaporation of the filtrate gave a syrup from which a few prisms crystallized after a time.

D-Arabitol: The prisms were hand-picked and recrystallized from water by the addition of acetone to give colourless prisms of D-arabitol, m.p. 101–102 °C, $[\alpha]_D^{22} +7.1^\circ$ (c, 7.8 in saturated borax solution). The product was readily soluble in water and gave a negative Molisch test.

In another experiment, evaporation of an acetone extract gave colourless prisms, m.p. 99.5–100 °C, readily soluble in water.

The above product was converted into penta-acetyl-D-arabitol, m.p. 75.5–76 °C from benzene-light petroleum.

(iii) *Usnea barbata* (L.) Wigg.—Milled lichen (505 g) was extracted successively with light petroleum, ether, and 70% aqueous methanol.

(1) *Light Petroleum Extract.* Evaporation gave (+)-usnic acid (3.8 g, 0.75%), $[\alpha]_D^{15} +500^\circ$ (c, 0.91 in CHCl_3), m.p. 203–204 °C, undepressed in admixture with reference material. The product from another sample was further identified by conversion into (+)-diacetylusnic acid, pale yellow needles from methanol, m.p. 200–201 °C, and by racemization.

(±)-*Usnic Acid:* The above product was refluxed in xylene solution. After 7 hr the material had m.p. 193–196 °C and $[\alpha]_D^{16} +110^\circ$ (c, 0.69 in CHCl_3); after 16 hr the product was (±)-usnic acid, m.p. 196–197 °C, the optical rotation in a 1 dm tube being $<0.02^\circ$ (c, 0.7 in CHCl_3).

(2) *Ether Extract.* Evaporation gave a yellowish residue which was extracted successively with benzene and ether in a Soxhlet extractor. Concentration of the benzene extract gave (+)-usnic acid (5.3 g, 1.05%), m.p. 203–204 °C, undepressed in admixture with reference material. Concentration of the ether extract gave a white powder (c. 1 g), m.p. 250–265 °C (decomp.), raised to a constant value of 270 °C (decomp.) on repeated recrystallization from aqueous acetone or isobutyl methyl ketone (Found: C, 56.8; H, 3.5; C-CH₃, 4.4%). Part of this material was acetylated by the method below to a product which melted at 166–167 °C, resolidified, and then melted at 207–211 °C. The residue from the Soxhlet extractions above had m.p. 270–290 °C (decomp.). This and the material extracted by ether were then found each to show a spot for salazinic acid and a somewhat stronger spot at higher R_F on paper chromatograms. The combined solids were suspended in cold ethanol (100 ml) and the mixture was filtered after 24 hr. No pure product was obtained from the filtrate.

Norstictic Acid: The residue insoluble in ethanol was recrystallized several times from 80% aqueous acetone to give small colourless needles of norstictic acid (85 mg, 0.017%), m.p. 282–283 °C (decomp.), with browning from c. 270 °C (Found: C, 58.3; H, 3.5%. Calc. for $\text{C}_{15}\text{H}_{12}\text{O}_8$: C, 58.2; H, 3.3%). The product was sparingly soluble in water and common organic solvents including dry acetone, but dissolved readily in boiling 80% aqueous acetone. With cold 2N

sodium hydroxide it gave a yellow solution which deposited red needles after being kept for some time. It gave a deep yellow colour with *p*-phenylenediamine.

Norstictic acid was converted into penta-acetylnorstictic acid, m.p. 212 °C, in a capillary tube; on a hot-stage under the microscope however the product softened in the range 208–212 °C, partly resolidified, then melted at 227 °C (Found: * C, 55.8; H, 4.3%. Calc. for $C_{28}H_{24}O_{15}$: C, 56.0; H, 4.0%).

(3) *Methanol Extract*. The syrup deposited a few colourless prisms of *D*-arabitol, m.p. 101–102.5 °C, and $[\alpha]_D^{22} + 7.7^\circ$ (c, 7.8 in saturated borax solution). Acetylation gave penta-acetyl-*D*-arabitol, m.p. 75 °C undepressed in admixture with the corresponding product from *Ramalina fraxinea*.

Extraction of another sample with light petroleum and ether gave (+)-usnic acid (1.76%), norstictic acid (0.044%), and salazinic acid (0.073%). Extraction with acetone then gave salazinic acid (1.32%).

(iv) *Usnea ceratina* Ach.—Milled lichen (1200 g) was extracted by the general procedure.

(1) *Light Petroleum Extract*. The first runnings were red in colour, but the red material remained in the waxy residue on evaporation of the solvent. Concentration of the extract gave (+)-usnic acid (1.6 g, 0.13%), $[\alpha]_D^{23} + 495^\circ$ (c, 0.72 in $CHCl_3$) and m.p. 201–202 °C undepressed in admixture with reference material.

(2) *Ether Extract*. Prolonged extraction and treatment as for the extract from *U. barbata* gave (+)-usnic acid (7.2 g, 0.60%) and norstictic acid (555 mg, 0.047%) (Found: C, 58.4; H, 3.5; OCH_3 , <0.5; $O-CH_3$, 8.1%. Calc. for $C_{18}H_{12}O_6$: C, 58.2; H, 3.3; $2 \times C-CH_3$, 8.1%).

(3) *Acetone Extract*. The residue (28.7 g, 2.4%) on evaporation gave salazinic acid, m.p. 260 °C (decomp.), from 80% aqueous acetone, contaminated with a little norstictic acid (paper chromatogram). The product from another extraction gave hexa-acetylsalazinic acid, m.p. 177 °C, undepressed in admixture with reference material.

(4) *Aqueous Methanol Extract*. Acetylation of the syrupy concentrate gave a few colourless prisms, m.p. 73–74 °C, from benzene–light petroleum and possibly penta-acetyl-*D*-arabitol.

III. ACKNOWLEDGMENTS

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CHEMISTRY OF AUSTRALIAN LICHENS

II. A NEW DEPSIDONE FROM *PARMELIA CONSPERSA* (EHRH.) ACH.

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[Manuscript received September 22, 1959]

Summary

A new compound, norlobaridone, from *Parmelia conspersa* is shown to have structure Ia by conversion of its monomethyl ether (lobaridone (Ib)) into lobariol (IIb). The depsidone ring is readily cleaved by basic reagents to give products containing a new cyclic system and including an isomeric γ -enol lactone (IIIa), norlobariol (IIa), and the oxime anhydride (IVa) of the latter. Ultraviolet and infra-red spectra support structural assignments. Norlobaridone (Ia) presents an exception to the acetate theory of biogenesis in the position of its ketonic oxygen atom.

I. INTRODUCTION

In Part I of this series, Briner, Gream, and Riggs (1960) described the isolation from *Parmelia conspersa* (Ehrh.) Ach. of compound P, m.p. 188 °C, not recorded in the literature. Compound P was assigned the probable molecular formula $C_{23}H_{26}O_6$, containing two terminal methyl groups but no methoxyl group. It was phenolic and formed a diacetyl derivative with acetic anhydride and sulphuric acid.

Results described below show that compound P has structure Ia. Structure Ia was shown by Asahina and Nonomura (1935) and Asahina and Yasue (1936, 1937) to represent lobaric acid, so that compound P is decarboxynorlobaric acid. We suggest however the more convenient and less misleading name, norlobaridone.

Structure Ia accounts for the formation of a tetrabromo derivative, for the Kuhn-Roth analytical value, and for the structurally more significant result that oxidation with potassium permanganate yields rather more than 1 mole of steam-volatile acids consisting of *n*-caproic acid together with smaller amounts of *n*-butyric and *n*-valeric acids. The formation and spectra (discussed below) of diacetylnorlobaridone (Id), now obtained with acetic anhydride and pyridine, and methyl-lobaridone (Ic) demonstrate the presence of only two hydroxyl groups, both phenolic, in the parent. Ultimate proof of structure Ia however rests on conversion by alkali of the monomethyl ether, best obtained by brief contact with diazomethane in ether, into lobariol (IIb), identical with a sample kindly provided by Professor S. Shibata. (The lactol structure for lobariol

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rather than the isomeric *o*-ketocarboxylic acid structure used by Asahina and Nonomura (1935) and Asahina and Yasue (1936, 1937) to interpret their otherwise unequivocal chemical results follows from spectral results discussed below.)

The monomethyl ether must be formulated as lobaridone (Ib), and its acetyl derivative as Ie. The preferential methylation is readily accounted for by the greater acidity of the hydroxyl group attached to ring S (=Säureglied; nomenclature of Asahina and Shibata (1954) for the corresponding ring in depsides) which carries also two electron-attracting carbonyl substituents. The value, pK_c 7.8, obtained by potentiometric titration of norlobaridone (Ia) in 50 per cent. aqueous ethanol is assigned to this hydroxyl group for, although no value for pK_2 was obtained, norlobaridone (Ia) required 1.05 equivalents of alkali to the end-point of phenolphthalein whereas lobaridone (Ib) required only 0.33 equivalent corresponding to acidity in the range for simple phenols (pK_c 10) (cf. Wachtmeister 1956).

Norlobaridone (Ia) was converted by hot sodium hydroxide solution into norlobariol (IIa), and by sodium methoxide solution into the corresponding pseudo-ester (IIc). The latter product was not obtained pure and retained water of crystallization; it may not however be formulated as norlobariol containing methanol of crystallization for, although it was obtained by Fischer-Speier esterification of norlobariol (IIa), the latter was unaffected by the action of sodium methoxide or by recrystallization from aqueous methanol. The pseudo-ester (IIc) yielded norlobariol (IIa) with aqueous alkali. The action of alkali and dimethyl sulphate on norlobaridone (Ia) or, better, norlobariol (IIa) gave dimethyl-lobariol (IIId), previously obtained by Asahina and Yasue (1936) and decarboxylated by them to an oily ketone. In the present work we have prepared the pseudo-anhydride, acetyldimethyl-lobariol (IIe), and characterized the oily ketone as its 2,4-dinitrophenylhydrazone whose light absorption provides incidental proof that the carbonyl group is adjacent to an aromatic nucleus (Braude and Jones 1945).

Less vigorous treatment of norlobaridone (Ia) with alkali or heating it alone above its melting point gave *isonorlobaridone*, also obtained by the action of boiling formic acid on norlobariol (IIa). *isonorlobaridone* formed a triacetyl derivative (IIIb) and, on ozonolysis, yielded *n*-butyraldehyde; it is therefore ascribed the enol-lactone structure (IIIa).

Hydroxylamine in aqueous ethanol or pyridine solution converted norlobaridone (Ia) or norlobariol (IIa) into the same nitrogen-containing derivative. The product was not a simple oxime or hydroxamic acid since it was stable to boiling dilute hydrochloric acid and gave no violet colour with ferric chloride. Analysis of the pure material obtained after some initial difficulties and its formation from norlobariol (IIa) show that it was norlobariol oxime anhydride (IVa), formulated by analogy with other oxime anhydrides (Brady *et al.* 1928). Asahina and Nonomura (1935) described the corresponding product from lobariol (IIb) as lobariol oxime, recording an analysis in approximate agreement; present results show that it was lobariol oxime anhydride (IVb), apparently retaining some water of crystallization.

Structures assigned to compounds described above are supported by the results of spectral measurements discussed below. We may here remark that norlobaridone (Ia) constitutes a second exception to the rule that a carbonyl group in a side chain in position 6 of ring S in a naturally-occurring depsidone lies in the β -position, the first exception noted by Birch (1957) being lobaric acid (If). We add that depsidones not containing a carboxyl or methoxycarbonyl group are of relatively rare natural occurrence; decarboxylation of a precursor to norlobaridone (Ia) under the mild conditions of its isolation is however unlikely, conditions under which lobaric acid (If) easily survives.

II. ULTRAVIOLET ABSORPTION SPECTRA

Ultraviolet absorption spectra in the readily accessible region above 220 $m\mu$ are presented in Table I.

Norlobaridone (Ia) and its methyl ethers (Ib and Ic) exhibit a single broad maximum centred around 270 $m\mu$ with rising absorption below 250 $m\mu$; the diacetyl derivative is anomalous in giving only two ill-defined inflexions. The latter spectrum resembles that of the orcinol depsidone, physodic acid (Hale 1956), shifted somewhat to shorter wavelengths.

TABLE I
ULTRAVIOLET ABSORPTION SPECTRA IN 95 PER CENT. ETHANOL

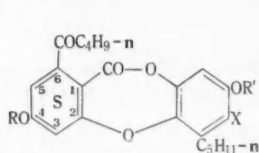
Compound	$\lambda_{\max.}$ ($m\mu$) Log ϵ (in parentheses)
Ia	270(3.96)
Ib	267(4.01)
Ic	268(3.96)
Id	250*(3.89), 292*(3.37)
IIa	259(4.15), 284(3.86), 290*(3.82)
IIb	256(4.20), 284(3.88), 291*(3.83)
IIc	260(4.19), 285(3.90), 292*(3.85)
IId	258(4.21), 284(3.86), 290*(3.81)
IIId†	252*(4.12), 281(4.02), 309(4.07)
IIE	261(4.19), 284(3.83), 294*(3.76)
IIIa	248(4.60), 281(4.22), 318(3.88), 332(3.89)
IIIb	238(4.55), 267(4.25), 320(4.03), 331(4.03)
IVa	239(4.60), 274*(4.01), 316(3.63), 328*(3.58)
IVb	239(4.63), 276*(3.97), 316(3.61), 328*(3.58)

* Shoulder.

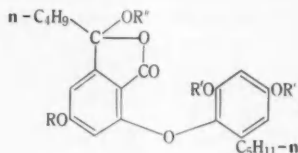
† In 0.05N sodium hydroxide in 95% ethanol.

Fission of the depsidone linkage and, except in one case, masking of the ketone group, result in spectra with rather more structure and between which useful comparisons may be drawn. Insofar as absorption may be assigned to individual chromophores the new double maximum in the 320–330 $m\mu$ region in the spectrum of isonorlobaridone (IIIa) is a function of the conjugated olefinic linkage being little affected by acetylation whereas the "aromatic" bands in the 250–280 $m\mu$ region suffer displacement by 10–15 $m\mu$ to shorter wavelengths. Removal of the olefinic linkage by hydration or analogous structural changes results in the

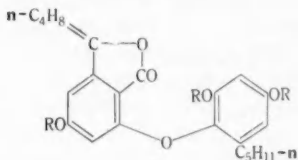
same type of spectrum shifted 20–40 $m\mu$ to shorter wavelengths, as shown in the spectra of norlobariol (IIa) and its functional derivatives. The close similarity in neutral 95 per cent. ethanol of the latter group, including especially the spectrum of acetyldimethyl-lobariol (IIe) shows that in this solvent all these compounds retain the lactol structures depicted. The substantially different spectrum of dimethyl-lobariol (IIId) in alkaline solution reflects ionization with opening of the lactol ring (Grove 1952).



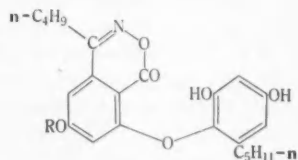
- (Ia): R = R' = X = H
 (Ib): R = Me; R' = X = H
 (Ic): R = R' = Me; X = H
 (Id): R = R' = Ac; X = H
 (Ie): R = Me; R' = Ac; X = H
 (If): R = Me; R' = H; X = CO₂H



- (IIa): R = R' = R'' = H
 (IIb): R = Me; R' = R'' = H
 (IIc): R = R' = H; R'' = Me
 (IIId): R = R' = Me; R'' = H
 (IIe): R = R' = Me; R'' = Ac



- (IIIa): R = H
 (IIIb): R = Ac



- (IVa): R = H
 (IVb): R = Me

Oximes of $\alpha\beta$ -unsaturated ketones absorb at practically the same wavelength as the parent ketones with relatively small changes up or down in intensity (Evans and Gillam 1943), and the same is no doubt true for aryl alkyl ketones and their oximes. For the hydroxylamine derivatives of norlobariol (IIa) and lobariol (IIb), the spectra of the parent lactols do not afford a valid reference, but the spectrum of dimethyl-lobariol (IIId) in alkaline solution, which probably resembles that of the unknown *o*-ketocarboxylic acids (Buu-Hoi 1941), does. Analyses aside, this comparison suggests that the present derivatives are not simple oximes. The spectra are in fact more closely comparable with those of isonorlobaridone (IIIa) and its triacetyl derivative (IIIb) with the longer wavelength bands reduced somewhat in intensity and that in the 270–280 $m\mu$ region appearing as a broad shoulder. The double maximum in the 320–330 $m\mu$ region might suggest structures having a conjugated exocyclic olefinic linkage instead of the endocyclic C=N linkage in those given (IVa and IVb). Brady *et al.* (1928) however recorded a broad single maximum at *c.* 330 $m\mu$ (which may not have been resolved with techniques then available) and a broad shoulder at *c.* 270 $m\mu$ in the spectrum of the oxime anhydride of opianic acid (6-formyl-

2,3-dimethoxybenzoic acid) in which an exocyclic double bond is not possible, and the analogous formulations, IVa and IVb, have been retained. In any event, the spectra of the present derivatives are so similar that there is no doubt they represent the same conjugated system. Finally, conversion of the norlobaridone derivative into the oxime anhydride does not occur during recrystallization from benzene for the spectrum of the crude product (once crystallized from aqueous ethanol) shows maxima and shoulders in the same position as given for the pure compound IVa in Table 1, but of slightly different relative intensities ($\Delta \log \epsilon \pm 0.05$).

TABLE 2
INFRA-RED ABSORPTION SPECTRA

Measured in Nujol mulls except where otherwise shown; only bands above 1620 cm^{-1} are shown; m, medium; s, strong; (br), broad; (r.sh), relatively sharp

Compound	$\lambda_{\text{max.}}$ (cm^{-1})
Ia	3250s(br), 1680s
Ib	3307s(br), 1683s
(in CCl_4)	3620s, 3400m(br), 1740s, 1710s
Ic	1728s, 1708s
(in CCl_4)	1745s, 1712s
Id	1760s, 1736s, 1703s
(in CCl_4)	1780s, 1750s, 1710m
Ie	1750s, 1730s, 1700s
IIa	3280s(br), 1723s
IIb	3350s, 1710s
(in KCl disk)	3320s(br), 1730s
IIc	3280s(br), 1720s
IId	3330m(r.sh), 1728s
IIf	1767s
IIIa	3280m(br), 1726s, 1680m
IIIb	1777s, 1683m
IVa	3210s(br), 1697s

III. INFRA-RED ABSORPTION SPECTRA

Solid state and, where measured, solution spectra all showed two strong absorption bands in the region $1585\text{--}1610 \text{ cm}^{-1}$ and attributed to aromatic nuclei, as well as various bands at lower frequencies. In Table 2 are collected results of measurements at higher frequencies. In the discussion, generalizations concerning structure and absorption frequency are taken from Bellamy (1958).

Scale models of the simple depsidone system with the usual bond lengths and angles for elements in the particular valence states concerned are not planar. Although the effect of decreased conjugation has not been taken into account such models are relatively unstrained. In norlobaridone (Ia) and lobaridone (Ib) in the solid state strong intermolecular hydrogen bonding as shown by the hydroxyl bands near 3300 cm^{-1} results in strong unresolved absorption near 1680 cm^{-1} unsuitable for structural diagnosis. The parent Ia is insoluble in carbon tetrachloride but the presence of two carbonyl functions is shown by the

solution spectrum of its methyl ether (Ib) and both spectra of the dimethyl ether (Ic). In each case the band at $1728\text{--}1745\text{ cm}^{-1}$ is assigned to the depsidone carbonyl group in agreement with the value (1733 cm^{-1} in Nujol) found by Dean, Erni, and Robertson (1956) and near the usual value for aromatic esters. The band at $1708\text{--}1712\text{ cm}^{-1}$ must be assigned to the ketonic carbonyl group. Aryl alkyl ketones normally absorb in the range $1680\text{--}1700\text{ cm}^{-1}$, but the ketonic carbonyl group in the present compounds may be shown by models or calculation (Braude and Sondheimer 1955) to be twisted out of the plane of the aromatic nucleus to which it is attached and in consequence it partakes more of the nature of an aliphatic ketonic group. The spectra of the acetyl derivatives (Id and Ie) show the ketone and depsidone bands as well as bands due to phenolic acetate groups in the range $1750\text{--}1780\text{ cm}^{-1}$.

The detection by infra-red spectroscopy of lactol structures for aromatic *o*-ketocarboxylic acids has been discussed in detail by Grove and Willis (1951), and the formulation of norlobariol (IIa) and its functional derivatives as lactols follows unequivocally from the spectral results in Table 2. Except for the acetyl derivative (IIe) in which no hydrogen bonding is possible and for which acetate and phthalide absorptions are superposed at 1767 cm^{-1} , absorption due to the phthalide carbonyl group occurs in the range $1720\text{--}1730\text{ cm}^{-1}$ and hydroxyl absorption near 3300 cm^{-1} , the key reference compound here being dimethylnorlobariol (IIId) in which the lactol provides the only hydroxyl group. Significantly none of the present spectra shows a band in the range $1680\text{--}1710\text{ cm}^{-1}$ corresponding to a hydrogen bonded or distorted aryl alkyl ketone group.

3-Methylenephthalide absorbs at 1780 cm^{-1} (Grove and Willis 1951) and the low value (1726 cm^{-1}) shown by the *n*-butyridenephthalide system in isonorlobaridone (IIIa) is a reflection of strong hydrogen bonding as shown also by the hydroxyl absorption at 3280 cm^{-1} . In triacetylisonorlobaridone (IIIb) the phthalide absorption frequency rises to 1777 cm^{-1} near that expected and where it is superposed on that due to the phenolic acetate groups. The medium intensity band at 1680 cm^{-1} in both spectra is apparently insensitive to hydrogen bonding and is attributed to the olefinic linkage. The absorption frequency is near the upper end of the range for conjugated olefinic bonds, which is consistent with the observations of Davison and Bates (1953) that absorption due to an olefinic bond in an isopropenyl ester lay 24 cm^{-1} higher than that of the parent olefine, and of Meakins (1953) that absorption due to an exocyclic olefinic bond that was part of a five-membered cyclic vinyl ether lay $10\text{--}15\text{ cm}^{-1}$ higher than that of the corresponding acyclic compound. The unassigned absorption at 1680 cm^{-1} in the spectrum of patulin (Grove 1951) may similarly be due to the conjugated double bond exocyclic to the five-membered ring and in this case part of a six-membered ring (Woodward and Singh 1949).

The spectrum of norlobariol oxime anhydride (IVa) contains bands due to hydroxyl absorption (3210 cm^{-1}) and hydrogen-bonded arylcarboxylate absorption (1697 cm^{-1}) but no bands clearly due to olefinic or $\text{C}=\text{N}$ absorption, and is not structurally diagnostic.

It may be noted that norlobaridone (Ia) and its derivatives with an intact depsidone linkage absorb strongly in the $1270\text{--}1290\text{ cm}^{-1}$ region (not shown

in Table 2) whereas other compounds in Table 2 do not. Strong absorption in the 1250–1300 cm^{-1} region for benzoates and phthalates has been assigned to a C—O stretching mode (Bellamy 1958).

IV. EXPERIMENTAL

Light petroleum used had b.p. 60–80 °C. All evaporations to dryness were conducted under reduced pressure from the water-bath. Melting points were determined on a hot-stage under the microscope or in one case in a Pyrex capillary, and are uncorrected. Samples for analysis were dried in a high vacuum at 80 °C for 2 hr, except as otherwise noted. Analyses were by the C.S.I.R.O. Microanalytical Laboratory under the direction of Dr. K. W. Zimmerman. Ultra-violet absorption spectra were determined in 95% ethanol on a Unicam SP 500 spectrophotometer. Infra-red spectra were determined in Nujol mull on a Perkin-Elmer Model 13 spectrophotometer, or in carbon tetrachloride solution on a Unicam SP 100 spectrophotometer by Dr. G. Eglinton at the University of Glasgow.

(a) *Tetrabromonorlobaridone*.—To norlobaridone (200 mg) in 70% aqueous ethanol (10 ml) was added dropwise a solution of bromine (1 ml) in 70% aqueous ethanol (10 ml). After 10 min water was added and the precipitate was filtered off, washed thoroughly with water, and recrystallized from aqueous ethanol (charcoal) to give silky needles, m.p. 201–202 °C, which were dried in a vacuum at 45 °C for 7 hr (Found: C, 38.9; H, 3.3; Br, 43.8%. Calc. for $\text{C}_{22}\text{H}_{22}\text{O}_4\text{Br}_4$: C, 38.7; H, 3.1; Br, 44.9%). It gave no precipitate when heated with ethanolic silver nitrate.

(b) *Oxidation of Norlobaridone*.—Norlobaridone dissolved in pure acetone was treated with small quantities of finely powdered potassium permanganate until a faint pink colour persisted for 30 min at room temperature. The mixture was filtered and the residue was washed with boiling water. The combined filtrate and washings were evaporated to remove acetone and the aqueous residue was acidified with dilute sulphuric acid. The mixture was steam distilled and the distillate was titrated with 0.01N sodium hydroxide to the phenolphthalein end-point (Found: 1.25 equiv. of volatile acid). The acids were liberated with sodium hydrogen sulphate solution, extracted with *n*-butanol and neutralized to bromophenol blue with 33% ethylamine solution. Paper chromatography of a sample on Whatman No. 1 paper in the descending technique by the method of Lindqvist and Storgards (1953) gave spots at the same R_F values (0.36, 0.48, and 0.62, respectively) as reference spots of *n*-caproic, *n*-valeric, and *n*-butyric acids run on the same paper, and in approximate relative intensities (visual only) of 3:1:2.

(c) *Diacetylnorlobaridone (Id)*.—Norlobaridone (100 mg), acetic anhydride (2 ml), and pyridine (1 ml) were kept together for 2 days at room temperature. The mixture was evaporated to dryness and the residue was recrystallized from aqueous ethanol to give colourless needles (75 mg), m.p. 102–103 °C, raised on recrystallization from ether–light petroleum to 104 °C undepressed in admixture with the derivative previously prepared with sulphuric acid as catalyst (Briner, Gream, and Riggs 1960).

(d) *Methyllobaridone (Ic)*.—An excess of ethereal diazomethane was distilled into a solution of norlobaridone (400 mg) in ice-cold methanol (20 ml). After 1 hr the mixture was evaporated to dryness and the residue was recrystallized from benzene–light petroleum to give lobaridone (Ib), m.p. 137–138 °C (100 mg). The mother liquors evaporated to dryness gave colourless needles (250 mg), m.p. 63–65 °C from aqueous methanol, raised to 68 °C on recrystallization from light petroleum (Found: C, 70.6; H, 7.0; OCH_3 , 14.4%. Calc. for $\text{C}_{25}\text{H}_{30}\text{O}_4$: C, 70.4; H, 7.1; $2 \times \text{OCH}_3$, 14.6%).

(e) *Lobaridone (Ib)*.—A solution of norlobaridone (1.00 g) in ether (20 ml) was treated with an excess of ethereal diazomethane for 10 min and evaporated to dryness. The residue formed needles (890 mg), m.p. 136–137 °C from aqueous ethanol, raised to 139–140 °C on recrystallization from benzene–light petroleum (Found: C, 69.9; H, 6.9; OCH_3 , 7.5%. Calc. for $\text{C}_{24}\text{H}_{28}\text{O}_4$: C, 69.9; H, 6.8; $1 \times \text{OCH}_3$, 7.5%). It gave a green colour with ferric chloride in chloroform–pyridine (Soloway and Wilen 1952) but no colour with ethanolic ferric chloride. The yield of lobaridone was lower after longer reactions time, being c. 80% after 20 min, c. 50% after 90 min, and c. 20% after 12 hr; no crystalline material was isolated from the mother liquors in the latter cases.

(f) *Lobarol (Iib)*.—A solution of lobaridone (555 mg) in 1N sodium hydroxide (15 ml) was heated on the water-bath for 1 hr. The yellow solution was cooled and acidified with hydrochloric acid, and the mixture was extracted with ether (3×20 ml). The red ether extract was washed with 5% sodium hydrogen carbonate solution (2×10 ml) and water (3×10 ml), and dried over sodium sulphate. The residue left on evaporation of the ether gave needles (425 mg), m.p. 168°C , from benzene-light petroleum (Asahina and Nonomura 1935 give m.p. 168°C , misprinted as 163°C in Asahina and Shibata 1954) (Found: C, 66.9; H, 7.1; OCH_3 , 7.2%. Calc. for $\text{C}_{24}\text{H}_{30}\text{O}_7$: C, 66.7; H, 7.0; $1 \times \text{OCH}_3$, 7.2%). The m.p. was not depressed on admixture with authentic lobarol, and the infra-red spectra of the two samples measured in potassium chloride disks were identical in all respects. The product was sparingly soluble in 5% sodium hydrogen carbonate solution and gave no colour with ethanolic ferric chloride; it gave a green colour with ferric chloride in chloroform-pyridine.

(g) *Acetyl-lobaridone (Ie)*.—A solution of lobaridone (100 mg) in acetic anhydride (2 ml) and conc. sulphuric acid (1 drop) was kept at room temperature for 2 days then poured onto ice. The product was washed thoroughly with water and dried in a vacuum desiccator. Several recrystallizations from light petroleum gave needles, m.p. 106°C , which were dried at 65°C in a high vacuum (Found: C, 68.9; H, 6.6; COCH_3 , 10.4%. Calc. for $\text{C}_{26}\text{H}_{30}\text{O}_7$: C, 68.7; H, 6.7; $1 \times \text{COCH}_3$, 9.4%).

(h) *Equivalent Weight and pK Determinations*.—Norlobaridone (23.7 mg) in ethanol (10 ml) required 15.12 ml of 0.00413N barium hydroxide for neutralization to the phenolphthalein end-point (Found: E , 380. Calc. for $\text{C}_{23}\text{H}_{26}\text{O}_6$: M , 398.4). The apparent pH at half-neutralization in 50% aqueous ethanol with a Cambridge glass electrode and pH-meter was c. 7.8, but the end-point was an indistinct inflexion and the second end-point was beyond the range of the glass electrode used. Acidification of these solutions with dilute hydrochloric acid gave back norlobaridone (Ia), m.p. and mixed m.p. 188°C . Lobaridone (30.1 mg) in ethanol (10 ml) required 5.90 ml of 0.00413N barium hydroxide for neutralization to the phenolphthalein end-point (Found: E , 124. Calc. for $\text{C}_{24}\text{H}_{28}\text{O}_6$: M , 412.5).

(i) *Norlobarol (IIa)*.—Norlobaridone (1.07 g) was heated on the water-bath with 1N sodium hydroxide (25 ml) for 2 hr. The reddish solution was acidified and the precipitate recrystallized from aqueous ethanol to give fawn needles (1.10 g), m.p. 187°C , raised to 192 – 192°C on further recrystallization (Found: C, 66.1; H, 6.9%. Calc. for $\text{C}_{23}\text{H}_{26}\text{O}_7$: C, 66.3; H, 6.8%). Norlobarol gave a bluish green colour with ferric chloride in chloroform-pyridine, but no colour with ethanolic ferric chloride. It was soluble in 5% sodium hydrogen carbonate solution but the sodium salt was insoluble in more concentrated solutions; saturation of a solution of norlobarol in 2N sodium hydroxide with carbon dioxide gave a precipitate soluble in water and yielding norlobarol on acidification with hydrochloric acid.

(j) *Norlobarol Methyl Pseudo-Ester (IIc)*.—(i) Norlobaridone (758 mg) was dissolved in c. 2N sodium methoxide in methanol (20 ml). After 2 hr at room temperature the mixture was acidified with glacial acetic acid and evaporated. The solid residue was washed thoroughly with water and recrystallized from aqueous methanol to give needles (620 mg), m.p. 115 – 120°C , unchanged on several recrystallizations. (For the isomeric normal ester Asahina and Nonomura (1935) give m.p. 140°C from methanol.) A sample dried at 80°C lost no weight when heated at 100°C in a vacuum for several hours (Found: C, 64.7; H, 7.2; OCH_3 , 6.6%. Calc. for $\text{C}_{24}\text{H}_{30}\text{O}_7 \cdot \text{H}_2\text{O}$: C, 64.3; H, 7.2; $1 \times \text{OCH}_3$, 6.9%). The product gave a green colour with ferric chloride in chloroform-pyridine, but no colour with ethanolic ferric chloride. It was insoluble in sodium hydrogen carbonate solution, and was recovered in 90% yield when its solution in 2N sodium hydroxide was acidified after 2.5 hr at room temperature. Refluxing a solution of the pseudo-ester (52 mg) in 2N sodium hydroxide (5 ml) for 2 hr, acidification, and recrystallization of the precipitate from aqueous ethanol gave needles (45 mg), m.p. 191 – 192°C , undepressed in admixture with norlobarol.

(ii) A solution of norlobarol (120 mg) in methanol (2.7 ml) and conc. hydrochloric acid (0.3 ml) was refluxed for 3 hr. Addition of water and recrystallization of the product from

* The acetic acid distillate was pink, and the end-point to phenolphthalein difficult to determine.

aqueous methanol gave needles (89 mg), m.p. 115–120 °C, alone or mixed with the product from (i) above.

Norlobarol was unchanged by treatment with sodium methoxide and acidification (85% recovery) and had m.p. 192–193 °C after recrystallization from aqueous methanol.

(k) *Dimethyl-lobarol (IId)*.—(i) Norlobaridone was refluxed with an excess of 2N sodium hydroxide for 2 hr. An excess of dimethyl sulphate dissolved in methanol was then added dropwise to the boiling mixture and the alkaline mixture was refluxed for a further hour. The methanol was evaporated and the mixture was acidified. The oil was extracted with ether, and the extract after being washed with sodium hydrogen carbonate solution and water was evaporated. The residue was remethylated and the oil was extracted as before. Chromatography on silica gel and elution with benzene–ether (9:1) gave a crystalline powder (c. 20%), m.p. 138–139 °C after several recrystallizations from benzene–light petroleum (Asahina and Yasue (1936) give m.p. 138 °C) (Found: C, 68.2; H, 7.6; OCH_3 , 19.5%. Calc. for $\text{C}_{24}\text{H}_{34}\text{O}_7$: C, 68.1; H, 7.5; $3 \times \text{OCH}_3$, 20.3%). The product gave no colour with ferric chloride in ethanol or in chloroform–pyridine.

(ii) Norlobarol (540 mg) was dissolved in methanol (20 ml) and dimethyl sulphate (2.0 ml) was added. The mixture was refluxed during dropwise addition of 1N sodium hydroxide (40 ml) and for 1 hr thereafter, then worked up and remethylated as before. The oily product without being chromatographed crystallized from benzene–light petroleum in warts (475 mg), m.p. 139 °C, alone or mixed with the product from (i) (Found: OCH_3 , 19.7%).

(l) *Acetyldimethyl-lobarol (IIe)*.—A mixture of dimethyl-lobarol (100 mg), acetic anhydride (2 ml), and pyridine (1 ml) was kept at room temperature for 2 days then evaporated to dryness. The residue on recrystallization from aqueous ethanol with norite formed needles (73 mg), m.p. 115–116 °C (Found: COCH_3 , 8.5%. Calc. for $\text{C}_{24}\text{H}_{34}\text{O}_8$: $1 \times \text{COCH}_3$, 8.6%).

(m) *Dimethyldecarboxylobarol*.—A solution of dimethyl-lobarol (60 mg) in purified quinoline (5 ml) was refluxed with copper powder (100 mg) for 30 min, then poured into hydrochloric acid. The ether extract (3×10 ml) was washed with dilute hydrochloric acid (3×10 ml), water (10 ml), 5% sodium hydrogen carbonate (2×10 ml), and water (2×10 ml), dried over sodium sulphate, and evaporated. The oily residue (Asahina and Yasue (1936) give b.p. 205–210 °C/0.01 mm, but do not characterize the product further) in methanol (2 ml) was treated with a solution of 2,4-dinitrophenylhydrazine sulphate in methanol. The precipitate recrystallized from ethanol, then light petroleum, formed orange fluffy needles, m.p. 140 °C (Found: C, 62.7; H, 6.6; OCH_3 , 15.4%. Calc. for $\text{C}_{23}\text{H}_{30}\text{O}_6\text{N}_4$: C, 62.6; H, 6.4; $3 \times \text{OCH}_3$, 15.7%). Light absorption in ethanol: λ_{max} , 378 m μ (broad band) $\log \epsilon$ 4.42.

(n) *isoNorlobaridone (IIIa)*.—(i) Norlobaridone (1.00 g) was dissolved in 2N sodium hydroxide (20 ml) at room temperature and, after 10 min, the mixture was acidified with dilute hydrochloric acid. The precipitate, recrystallized from aqueous acetone, gave needles (650 mg), m.p. 246–248 °C, raised to 250–251 °C on recrystallization from aqueous ethanol (Found: C, 69.4; H, 6.8%. Calc. for $\text{C}_{23}\text{H}_{30}\text{O}_6$: C, 69.3; H, 6.6%). The product gave a green colour with ferric chloride in chloroform–pyridine but no colour with ethanolic ferric chloride, and was insoluble in 5% sodium hydrogen carbonate solution.

(ii) Norlobaridone (200 mg) was heated in a Pyrex tube at 220 °C for 30 min. Cooling and recrystallization of the red product from aqueous ethanol with addition of norite gave colourless needles (120 mg), m.p. 245 °C, raised on recrystallization to 248–250 °C, undepressed in admixture with the product from (i) above.

(iii) Norlobarol (200 mg) was refluxed with 98–100% formic acid for 2 hr. Evaporation to dryness and recrystallization of the residue from aqueous ethanol gave needles (120 mg), m.p. 249–250 °C, undepressed in admixture with the product from (i) above.

(o) *Triacetylisonorlobaridone (IIIb)*.—*iso*Norlobaridone (118 mg), acetic anhydride (2 ml), and freshly fused sodium acetate (100 mg) were heated together on the water-bath for 4 hr. The mixture was poured into water (50 ml) and solid sodium hydrogen carbonate (c. 1 g) was added to neutralize acetic acid. The oil solidified and formed flat plates (86 mg) from aqueous ethanol, m.p. 78–80 °C in a capillary tube. The compound softened and liberated volatile acids (odour) at 70 °C; it was dried in a vacuum at 50 °C for 2 hr (Found: C, 66.5; H, 6.2; COCH_3 , 25.0%. Calc. for $\text{C}_{20}\text{H}_{28}\text{O}_6$: C, 66.4; H, 6.2; $3 \times \text{COCH}_3$, 24.6%).

Only uncrystallizable oils were obtained when conc. sulphuric acid or pyridine was used instead of sodium acetate as catalyst.

(p) *Ozonolysis of isoNorlobaridone*.—A stream of ozonized oxygen was passed into a solution of isonorlobaridone (106 mg) in acetic acid (15 ml) at room temperature for 30 min. Zinc dust (2 g) and water (30 ml) were added and the mixture was steam distilled into a solution of 2,4-dinitrophenylhydrazine in dilute perchloric acid. The precipitate was recrystallized from ethanol to give orange needles (24 mg), m.p. 119–120 °C, undepressed in admixture with authentic *n*-butyraldehyde 2,4-dinitrophenylhydrazone. On paper chromatograms prepared by a modification (descending technique) of the method of Huelin (1952), the crude and purified products each gave a single spot at R_f 0.52. Reference spots of the 2,4-dinitrophenylhydrazones of *n*-propionaldehyde, *n*-butyraldehyde, and *n*-valeraldehyde run on the same paper had R_f 's of 0.43, 0.52, and 0.60 respectively.

(q) *Norlobariol Oxime Anhydride (IVa)*.—(i) A solution of norlobaridone (545 mg), hydroxylamine hydrochloride (1.00 g), and crystalline sodium acetate (1.00 g) in 50% aqueous ethanol (10 ml) was refluxed for 3 hr. Addition of water and recrystallization of the product from aqueous ethanol gave glistening flat needles (552 mg) which melted at 105 °C, resolidified at c. 130 °C, and remelted at 230–232 °C, behaviour which was unchanged on five recrystallizations from aqueous ethanol. The product was dried in a vacuum desiccator over conc. sulphuric acid for 5 days (Found: C, 61.7; H, 7.2; loss in a vacuum at 60 °C, 1.6%. Calc. for $C_{22}H_{31}O_6N$: C, 61.5; H, 7.0; $0.4H_2O$, 1.6%). The behaviour on heating was unchanged when the product was dried in a vacuum at 80 °C for 2 hr (Found: C, 65.0; H, 7.0; N, 3.1%; no loss in a vacuum at 140 °C. Calc. for $C_{22}H_{29}O_7N$: C, 64.0; H, 6.8; N, 3.2%). The product was then recrystallized from benzene and dried in a vacuum at 80 °C for 2 hr (Found: C, 67.0; H, 6.7%. Calc. for $C_{22}H_{27}O_7N$: C, 66.8; H, 6.6%). It had m.p. 232 °C, unchanged on recrystallization from aqueous ethanol. It gave a brown colour with ferric chloride in chloroform-pyridine but no colour with ethanolic ferric chloride. A solution of the compound in a mixture of equal volumes of 2*N* hydrochloric acid and dioxan was refluxed for 1 hr. Addition of water and cooling gave the oxime anhydride (c. 80%), m.p. and mixed m.p. 230 °C.

(ii) Norlobaridone was refluxed with twice its weight of hydroxylamine hydrochloride in pyridine solution for 3 hr. The reaction mixture was worked up by acidification and extraction with ether, the extract being washed with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water, and evaporated. The product (75% yield after recrystallization from aqueous ethanol, then benzene) had m.p. 232 °C alone or mixed with product from (i) above.

(iii) Norlobariol gave c. 80% yield of the same product (m.p. and mixed m.p.) by either method (i) or method (ii) above.

(r) *Lobariol Oxime Anhydride (IVb)*.—Lobariol (127 mg) was treated by method (i) for norlobariol oxime anhydride. The crude product after one crystallization from aqueous ethanol formed needles (103 mg), m.p. 155–160 °C, raised to 173–174 °C with softening above 60 °C after several recrystallizations from benzene (Asahina and Nonomura (1935) give m.p. 173 °C for "lobariol oxime"). The product was dried in a vacuum at 55 °C for 2 hr (Found: C, 66.3; H, 6.9; N, 3.0%. Calc. for $C_{22}H_{29}O_6 \cdot 0.5H_2O$: C, 66.0; H, 6.9; N, 3.2%).

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THE CHEMISTRY OF ANTS

III. STRUCTURE AND REACTIONS OF IRIDODIAL

By G. W. K. CAVILL* and D. L. FORD*

[Manuscript received December 7, 1959]

Summary

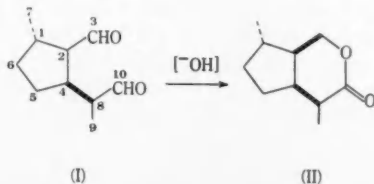
Iridodial, isolated from *Iridomyrmex detectus* (F.Sm.), is shown to be α -(2-formyl-3-methylcyclopentyl)propional (I). Iridodial exhibits 1,5-dialdehyde-lactol tautomerism. On the basis of spectroscopic and degradative studies, it is suggested that structures Ia and VIIIa contribute to a major extent in the tautomer distribution. Iridodial, on treatment with alkali, undergoes a Cannizzaro reaction to yield a mixture of lactones including isoiridomyrmecin and the dihydronepetalactones. The known nepetalinic acids (IIIa, b), together with two new nepetalinic acids (IIIc, d), are obtained by permanganate oxidation of the various lactone fractions. The conversion of iridodial into the pyridine alkaloid, actinidine, establishes a further relationship in the cyclopentanoid monoterpenes.

I. INTRODUCTION

The isolation and characterization of iridodial, from the Australian ant species, *Iridomyrmex detectus* (F.Sm.) and *I. conifer* (Forel), have been described in Part I of this series (Cavill, Ford, and Locksley 1956a), and following upon the conversion of this novel dialdehyde into isoiridomyrmecin (iridolactone), iridodial was formulated as α -(2-formyl-3-methylcyclopentyl)propional (I) (Cavill, Ford, and Locksley 1956b). It is now intended to discuss in detail the structure and reactions of iridodial. Iridodial has also been isolated in Italy from the ant, *Tapinoma nigerrimum* (Nyl), by Trave and Pavan (1956), and these workers express agreement with structure I.

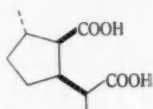
II. STRUCTURE OF IRIDODIAL

The characterization of iridodial ($C_{10}H_{16}O_2$) as the bis-2,4-dinitrophenylhydrazone, and as the disemicarbazone, together with its ready oxidation to yield a mixture of stereoisomeric dicarboxylic acids ($C_{10}H_{16}O_4$), confirms the presence of two aldehydic functions (cf. Part I, loc. cit.). A Kuhn-Roth estimation indicates the presence of two C-methyl groups. Our inability to hydrogenate iridodial under normal conditions, using Raney nickel or Adams's

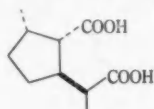


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catalyst, suggested the presence of a cyclic structure, rather than an unsaturated linear one. However, hydrogenation for a longer period (24 hr) led to the slow uptake of approximately one-third of a molecular proportion of hydrogen, and this absorption is ascribed to a partial reduction of the carbonyl function.



(IIIa)



(IIIb)

Normal aqueous sodium hydroxide solution readily isomerizes iridodial to a complex mixture of δ -lactones, which includes *isoiridomyrmecin* (iridolactone) (II), whose structure has been determined (Cavill and Locksley 1957). On oxidation *isoiridomyrmecin* yields the nepetalinic acid (IIIa) previously obtained from nepetalactone (IVa) (McElvain and Eisenbraun 1955; Bates, Eisenbraun, and McElvain 1958).

TABLE I
THE L-NEPETALINIC ACIDS AND THEIR DI-*p*-BROMOPHENACYL ESTERS

Acid*		Ester	
Melting Point (°C)	$[\alpha]_D$ (in CHCl_3)	Melting Point (°C)	$[\alpha]_D^{20}$ (in CHCl_3)
85 (IIIa)† 117–118§	+30† +14§	72‡ —	–109‡ —
115 (IIIb)† 111†	+19† —	124–126‡ —	+14‡ —
132 (IIIc)‡ (dimorphous 118) 120–120.5 (IIId)‡	+27‡ +36‡	134‡ —	+6.7‡ —

* Each of the above pairs of acids is epimeric at C_8 .

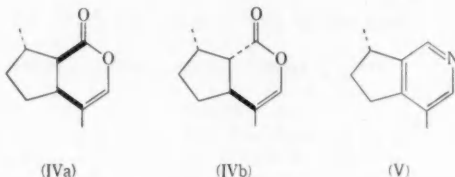
† McElvain and Eisenbraun (1955).

‡ Present work.

§ Cavill and Locksley (1957).

Iridodial, on direct oxidation with potassium permanganate/sodium hydrogen carbonate in acetone solution, yields the same nepetalinic acid (IIIa), together with a stereoisomer, presumably IIIb (Trave and Pavan 1956). Previously, we had reported (Part I, loc. cit.) that a potassium permanganate oxidation, in aqueous sodium hydroxide solution, gave a benzene-soluble dicarboxylic acid fraction ($\text{C}_{10}\text{H}_{16}\text{O}_4$), from which the major constituent was isolated as the di-*p*-bromophenacyl ester. A direct comparison of this derivative with the di-*p*-bromophenacyl ester of nepetalinic acid (IIIb) identifies the original dicarboxylic acid (see Table 1).

These inter-relations with *isoiridomyrmecin* and *nepetalactone* establish structure I for *iridodial*, whilst the *trans*-1,3- relation of the methyl and propionic acid substituents is confirmed in each of the *nepetalinic acids* (IIIa, IIIb) isolated on oxidation.



III. CONVERSION OF IRIDODIAL INTO ACTINIDINE

The quantitative conversion of *iridodial* into its bis-2,4-dinitrophenylhydrazone, results in a product which is chromatographically, and presumably stereochemically, homogeneous. However, attempts to establish the configuration of this derivative, by direct oxidation to a known *nepetalinic acid*, have been unsuccessful.

The bis-2,4-dinitrophenylhydrazone is converted into 1',5-dimethyl-3,4-*cyclopentenopyridine* (V) by the action of hydrochloric acid in acetic acid solution. This transformation, which confirms the 1,5-dicarbonyl relationship in *iridodial*, also provides a new synthesis for pyridine derivatives.* The ultraviolet spectrum of 1',5-dimethyl-3,4-*cyclopentenopyridine* has a major absorption band at 262 m μ (ethanol), which is in agreement with the calculated absorption for a 3,4,5-trialkylpyridine, λ_{max} 264 m μ (Podall 1957). The parent 3,4-*cyclopentenopyridine*, which has been isolated recently from a coal-tar fraction (Arnall 1958), has λ_{max} 261 m μ (Prelog and Metzler 1946).

More recently, Sakan *et al.* (1959) have reported that the picrate of our dimethyl-*cyclopentenopyridine* (V) is identical with the picrate of *actinidine*, a new terpene alkaloid obtained from the Japanese plant, *Actinidia polygama*. *isoiridomyrmecin* (*iridolactone*) has been isolated from the same plant.

IV. TAUTOMERISM OF IRIDODIAL

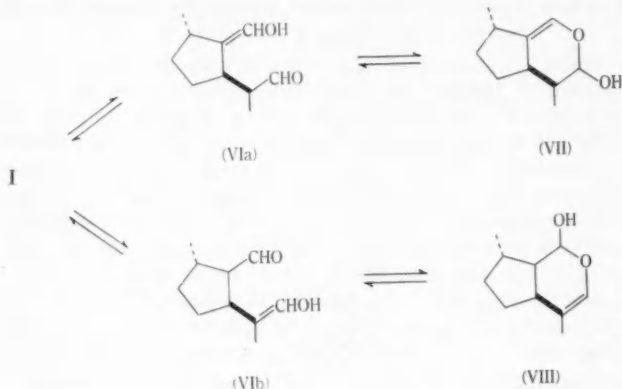
Structure I for *iridodial* has been established on the basis of chemical transformations, but physical constants indicate that the 1,5-dialdehyde form is in equilibrium with cyclic tautomers of the type VII and/or VIII.

The infra-red spectrum, in carbon tetrachloride solution, shows strong absorption at 3610 cm^{-1} indicative of the hydroxyl group, and absorptions at 3050, 1675, and 852 cm^{-1} indicative of the presence of trisubstituted ethylene (Bladon *et al.* 1951), thus confirming the lactol structures (VII, VIII). In support, *iridodial* gives a yellow colour with tetranitromethane in chloroform solution (cf. hydrogenation). Absorptions at 2710 and 1725 cm^{-1} are indicative of the open-chain 1,5-dialdehyde form, but *iridodial* gives an anomalous Schiff's

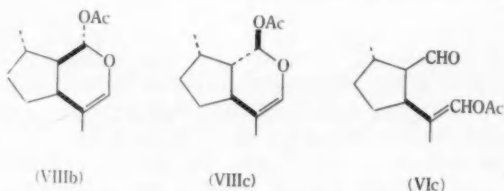
* Further applications of this method will be described in a subsequent paper.

test: the slow development of a blue colour, indicating the masking of the free aldehyde groups.

Again, a freshly distilled specimen of iridodial showed rapid mutarotation in benzene solution, stabilizing in 1 hr, $[\alpha]_D^{20} +4.7^\circ$ (c , 1.45 in benzene). Subsequently, Trave and Pavan (1956) reported $[\alpha]_D^{20} +67.7^\circ$ (c , 8.05 in methanol), and there is no doubt that the different rotation can be attributed to solvent effects, indicating not only a different tautomer distribution in

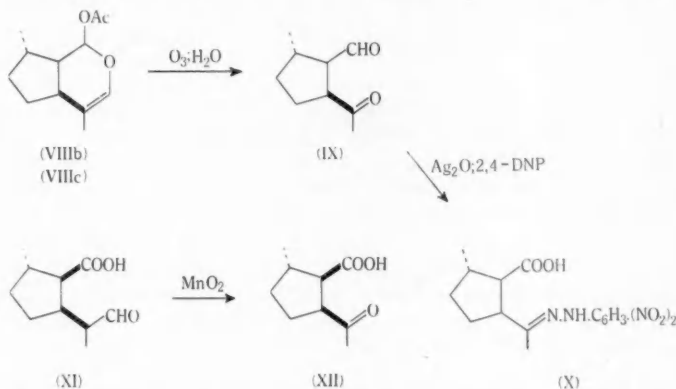


methanol, but also, the possibility of acetal formation. The molecular refraction (Lorentz-Lorenz) 47.5, which has been determined on the freshly distilled compound ($\frac{1}{2}$ hr) (cf. Part I), fits the lactol (calc. 47.2), rather than the dialdehyde (calc. 46.2), tautomer. Chemical confirmation of the lactol structure is given by the reaction of iridodial with acetic anhydride, which yields a monoacetate, formulated as a mixture of (VIIIb, VIIIc) on conformational grounds.

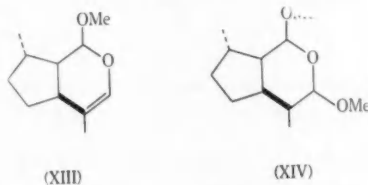


The infra-red spectrum, in carbon disulphide solution, shows the presence of trisubstituted ethylene (3050 , 1685 , 835 cm^{-1}), whilst the major carbonyl absorption is that of the acetate ester (1755 cm^{-1}). A shoulder at 1715 cm^{-1} is attributable to hydrolysis product/s. A monoenol acetate formulation (type VIc) is excluded, as there is no absorption $\sim 1780\text{ cm}^{-1}$ characteristic of a vinyl acetate (cf. Barnes *et al.* 1944). The lactol acetate readily yields a mixture of lactones and acetic acid on reaction with aqueous sodium hydroxide solution.

Ozonolysis of the lactol acetate (type VIII), in carbon tetrachloride solution at 0 °C, yielded an ozonide gum, and after decomposition with water, the product gave: (i) a strong pyrrole pine splint test on reaction with ammonium acetate (iridodial gives no reaction); (ii) an immediate copious precipitate of iodoform with sodium hypoiodite; and (iii) a yellow precipitate with aqueous 2,4-dinitrophenylhydrazine sulphate solution. On the basis of these qualitative tests, the ozonolysis product is formulated as 3-methyl-2-formylcyclopentyl methyl ketone (IX), thus supporting structure VIII for the lactol acetate. The ozonolysis product IX, which is partly soluble in water, was readily oxidized to a nepetonic



acid with moist silver oxide, the compound being isolated as the 2,4-dinitrophenylhydrazone (X). This yellow oil, soluble in dilute sodium hydrogen carbonate solution, did not crystallize over a period of 3 years. Bates, Eisenbraun, and McElvain (1958) have reported that the 2,4-dinitrophenylhydrazone of the nepetonic acid (assigned formula XII), obtained on oxidation of *cis,trans*-nepetalic acid (XI) with manganese dioxide, behaved similarly.

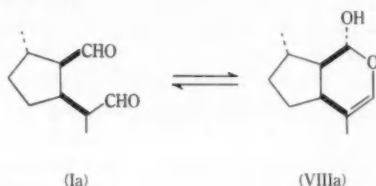


Iridodial, on treatment with methanol containing a trace of hydrogen chloride, yields a product whose infra-red spectrum shows absorptions at 1670 and 790 cm^{-1} , characteristic of trisubstituted ethylene, and at 1025 and 1120 cm^{-1} , attributable to ether oxygen. Additional bands at 1352 and 855 cm^{-1} are assigned to the methoxyl and methyl acetal groups, respectively, whilst the band at 1200 cm^{-1} is characteristic of a vinyl ether (cf. Potts and Robinson 1955). The product, which is not analytically pure (methoxyl estimation

indicates the presence of between one and two methoxyl groups), is a mixture of the methyl acetals (XIII, XIV). Similarly, Hall (1954) has shown that 1,5-dialdehydes with an unsubstituted α -position yield a mixture of the 2-methoxy-2,3-dihydropyran and the 2,6-dimethoxytetrahydropyran. Thus the ready formation of the lactol acetates (VIIIb, VIIIc), and of the methyl acetals (XIII, XIV), supports the physical evidence for 1,5-dialdehyde-lactol tautomerism. It is probable that both the *cis,trans*- and the *trans,cis*-lactol structures (type VIII) contribute to the tautomer equilibrium.

V. FURTHER OXIDATION REACTIONS

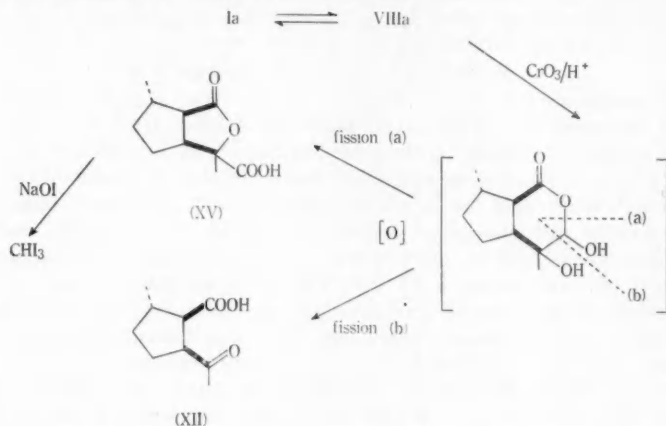
Permanganate oxidation of iridodial, in aqueous or in acetone solution, has yielded the nepetalinic acids (IIIa, IIIb) (see Section II). Now, manganese dioxide selectively oxidizes 2-hydroxytetrahydropyran to δ -valerolactone (Highet and Wildman 1955), and an equivalent transformation of the lactol tautomers of iridodial would yield the nepetalactones (type IV). However, iridodial, on mild oxidation with manganese dioxide (pH 5-6) in light petroleum, has given the nepetalinic acid (IIIa), together with a small proportion of an unidentified keto acid (cf. conversion of XI into XII). Excess iridodial was recovered. These results indicate that the oxidation, although mild, involved the dialdehydic form and as the *cis,trans*-nepetalinic acid (IIIa) was isolated, it is inferred that this series (Ia, VIIa) contributes to the major extent in the tautomer distribution. Comparably, Bates, Eisenbraun, and McElvain (1958) have shown that the *cis,trans*-nepetalactone (IVa) is the major, and the *trans,cis*-isomer (IVb) a minor, constituent of catnip.



Oxidation of iridodial with chromic acid in 3N sulphuric acid at 70 °C was vigorous, yielding carbon dioxide, acetaldehyde (isolated as the 2,4-dinitrophenylhydrazone), acetic acid (isolated as the *p*-bromophenacyl ester), and a $C_8H_{14}O_3$ keto acid, also isolated as the 2,4-dinitrophenylhydrazone. A viscous mixture of $C_{10}H_{16}O_4$ dicarboxylic acids, which remained, was characterized as the *N*-phenylimides. A material balance showed that a considerable proportion of the oxidation product was present as a green chromium complex, insoluble in hot 10N hydrochloric acid but decomposed on oxidation of the trivalent chromium to chromate with alkaline hydrogen peroxide solution. Paper chromatography of the product, after ether extraction, indicated a mixture of mono- and dicarboxylic acids, which gave a positive iodoform reaction, but no precipitate with 2,4-dinitrophenylhydrazine sulphate solution. Treatment with methanol, in the presence of hydrogen chloride, gave a methyl ester mixture, showing a strong absorption at 1785 cm^{-1} , typical of a γ -lactone. This band is

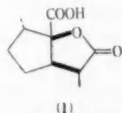
reduced by 95 per cent. when the ester mixture is treated with hypoiodite.* Especial interest attaches to the formation of the γ -lactonic acid, which must have a *cis*-relationship of the introduced hydroxyl group, and the carboxyl group, involved in lactonization (cf. structure XV).

Then the keto acid ($C_9H_{14}O_3$), isolated from the same oxidation, may be assigned the *cis,trans*-nepetonic acid structure (XII).

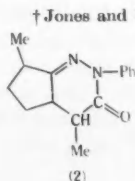


Since the isolation of this keto acid as its 2,4-dinitrophenylhydrazone, m.p. 168 °C, McElvain and his colleagues (loc. cit.) have reported the formation of the 2,4-dinitrophenylhydrazones of the *trans,trans*-nepetonic acid (XIIa), m.p. 174–175 °C, and of the *trans,cis*-compound (XIIb), m.p. 171–172 °C. Each of these 2,4-dinitrophenylhydrazones depresses the melting point of the derivative of the keto acid, m.p. 168 °C. Originally it appeared that this keto acid may have structure XVI, in which all active centres may be racemized, and accordingly, α -(2-oxo-3-methylcyclopentyl)propionic acid has been synthesized (cf. Jones and Linstead† 1936). But the 2,4-dinitrophenylhydrazone of XVI has m.p. 226 °C,

* As a small proportion of lactonic acid is not oxidized by the hypoiodite reaction.

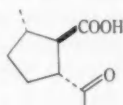


compound 1 contributes to a minor extent to the mixture.

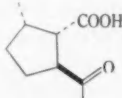


† Jones and Linstead characterized this keto acid (XVI) as the "phenylhydrazone", m.p. 192 °C (no analysis). However, reaction of our keto acid with phenylhydrazine gave a compound, m.p. 198.5 °C, from benzene, which is insoluble in dilute sodium hydroxide solution. This product is not the phenylhydrazone, but 1',4'-dimethyl-2-phenyl-5,6-cyclopentano-3[2H]-pyridazone (2), and the infra-red spectrum confirms this assignment. The cyclization of γ -keto acids to 3[2H]-pyridazones is well known (cf. Kucherov 1950).

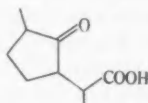
and depresses on admixture with XII. Thus considerable indirect support is given to the assigned structure XII for the C_9 keto acid, obtained from iridodial by oxidation.



(XIIa)



(XIIb)

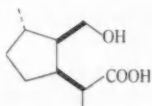


(XVI)

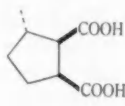
VI. THE 1,5-DIALDEHYDE- δ -LACTONE REARRANGEMENT

Iridodial undergoes a Cannizzaro reaction on warming with N potassium hydroxide in 90 per cent. alcoholic solution and, on adjustment to pH 5, a sparingly soluble δ -hydroxy acid is precipitated (53 per cent. yield). This compound, δ -(2-hydroxymethyl-3-methylcyclopentyl)propionic acid (XVII) was readily lactonized* to give *isoiridomyrmecin* [lactone fraction (1)], identical with an authentic specimen from *I. nitidus* (Part II, loc. cit.). The product, on oxidation with alkaline potassium permanganate solution, gave the nepetalinic acid (IIIa), characterized as the di-*p*-bromophenacyl ester, $[\alpha]_D^{20} -109.5^\circ$.

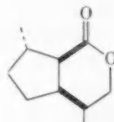
Fractional lactonization of the remaining δ -hydroxy acids gave lactone/s (2) in small yield, then lactone/s (3) (12 per cent. yield). Lactone fractions (2) and (3), on oxidation, gave the nepetalinic acid (IIIa), and fraction (3) also gave some *cis*-nepetic acid (XVIII). Thus fractions (2) and (3) contain the dihydro-



(XVII)



(XVIII)



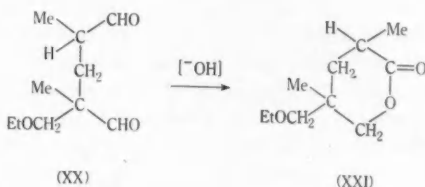
(XIX)

nepetalactones (XIX, epimeric at C_8), which are structural isomers of the iridomyrmecins. The crude lactone mixture shows an absorption at 1730 cm^{-1} , and at 1761 cm^{-1} (cf. the iridomyrmecins $\sim 1760\text{ cm}^{-1}$), and the former band has been reported for the dihydronepetalactones (Meinwald 1954).

The preponderance of *isoiridomyrmecin* (53 per cent.) compared with the dihydronepetalactones (12 per cent.) is attributed to a specificity in the direction of hydride ion transfer in the Cannizzaro reaction, and possibly to steric factors. Similarly, DeJong (1951) has reported that the dialdehyde (XX) yields predominantly the δ -lactone (XXI).

* This procedure effectively separates *isoiridomyrmecin* as the hydroxy acid (XVII), free from stereoisomers (see Part II).

The difficultly lactonizable hydroxy acids, remaining after the separation of fractions (1, 2, and 3), form lactone fraction (4) by distillation under reduced pressure. On oxidation with potassium permanganate solution, lactone fraction (4) yields nepetalinic acid (IIIb), and a new acid (IIIc). A repetition of the Cannizzaro reaction on iridodial, under more vigorous conditions, gave a comparable mixture of δ -lactones. In addition, fractional crystallization of the product obtained by oxidation of a lactone fraction (equivalent to 4), yields nepetalinic acid (IIIc), and a new acid IIId. The assignment of nepetalinic acid structures to IIIc and IIId rests on their formation from iridodial. Also, nepetalinic acid (IIIc) was converted into its dimethyl ester, then epimerized with sodium

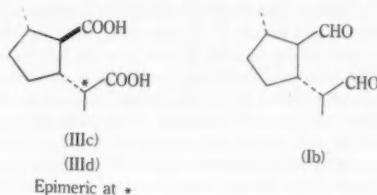


methoxide in methanol to yield the nepetalinic acid (IIId), m.p. 119–120.5 °C, identical with the acid, m.p. 120–120.5 °C, obtained on oxidation. Nepetalinic acid (IIIc) would appear dimorphous, m.p. 132 °C (117–119 °C), and has $[\alpha]_D^{23} +27^\circ$ (chloroform). Very recently, Sir Robert Robinson and his colleagues (Clark *et al.* 1959) reported the conversion of synthetic D-iridodial into a mixture of lactones including D-isoiridomyrmecin, and on oxidation, this mixture yielded a nepetalinic acid, m.p. 142 °C, $[\alpha]_D^{28} -16^\circ$ (chloroform). It is likely that this compound is the optical antipode of our "natural" acid, m.p. 132 °C. The di-*p*-bromophenacyl ester of (IIIc) has m.p. 134 °C, whilst the derivative of the synthetic acid (D-series) has m.p. 136–138 °C (Clark *et al.* 1959).

Sterically, acids IIIc, IIId differ from the known nepetalinic acids (types IIIa, IIIb, McElvain and Eisenbraun 1955), which exhibit a *cis,trans*- and a *trans,cis*-relation of the propionic acid, carboxyl, and methyl substituents, respectively. The new acids are assigned a *trans,trans*-configuration, and as with the other two pairs (see Table 1) are epimeric at C₈. Stereoisomers having a *cis,cis*-relation of the three adjacent substituents on the cyclopentane nucleus would be most unlikely from an epimerization reaction (cf. Jacobs and Florsheim 1950). Thus of the eight stereoisomers of nepetalinic acid which are theoretically possible, six have now been described.

A *cis*-relation of the propionic acid and methyl substituents is found only in IIIc and IIId: acids which are isolated in minor proportion. Such an inversion of configuration at C₄ may be attributed to a *retro*-Michael reaction, followed by the reformation of iridodial prior to the expected Cannizzaro rearrangement. The alternative that a small proportion of iridodial (Ib), having a *cis*-relation of the propional and methyl substituents, is present in the natural product is most unlikely. Thus the major proportion of the rearrangement product (lactone fractions 1, 2, and 3) (70 per cent. approx.) has a *cis*-fusion

of the cyclopentane and lactone nuclei, and is in accord with structures Ia \rightleftharpoons VIIIa for iridodial. A comparable steric relationship exists for the model compound, bisnoriridodial, which on treatment with alkali gives *cis*-bisoriridolactone (75 per cent.) (Hinterberger 1959, unpublished data).



VII. EXPERIMENTAL

Melting points are uncorrected. Light petroleum has b.p. 40–60 °C. The majority of the specific rotations were determined in a "Hilger" 0.5 dm microcell (capacity 0.3307 ml). Infra-red spectra were determined on a Perkin-Elmer Model 21 spectrometer with sodium chloride optics. Chromatographic alumina was prepared as previously reported in Part II. Organic solvent extracts were dried over anhydrous magnesium sulphate. Carbon, hydrogen, and nitrogen microanalyses are by Dr. E. Challen and Mr. D. Weedon of this University. Additional microanalyses are by Dr. K. W. Zimmerman and assistants, C.S.I.R.O. and University of Melbourne Microanalytical Laboratory.

(a) *1',5'-Dimethyl-3,4-cyclopentenopyridine*.—Iridodial bis-2,4-dinitrophenylhydrazine (200 mg) was suspended in hot acetic acid (5 ml; 17N), and hydrochloric acid (1 ml; 10N) added. The resultant brown solution was refluxed (2 hr), cooled, then adjusted to pH 9 with 2N sodium hydroxide solution. A sweet basic odour was noticeable. Steam distillation of the alkaline solution liberated a base (50 mg), isolated by extraction with chloroform. The base was subjected to a further steam distillation (from 2N sodium hydroxide solution), and re-extracted into chloroform. Removal of the solvent yielded a colourless oil (35 mg), which on treatment with a saturated aqueous picric acid solution, precipitated *1',5'-dimethyl-3,4-cyclopentenopyridine picrate* (57 mg), as golden prisms, m.p. 146–147 °C, insoluble in water, sparingly soluble in ethanol, but soluble in chloroform, $[\alpha]_D^{16} +46^\circ$ (c, 1.87 in CHCl_3) (Found: C, 51.0; H, 4.2; N, 14.7%. Calc. for $\text{C}_{18}\text{H}_{18}\text{O}_7\text{N}_4$: C, 51.1; H, 4.3; N, 14.9%).

The free base was regenerated on passing a solution of the picrate, in 95% ethanol, through a "Permutit FF" anionic exchange resin (-OH form, washed in 95% ethanol). The ultraviolet absorption spectrum in 95% ethanol, showed λ_{max} 262 m μ (ϵ 2590) and λ_{max} 270 m μ (ϵ 2310).

(b) *Reaction of Iridodial with Acetic Anhydride*.—Iridodial (0.414 g) was refluxed with acetic anhydride (2 ml) for 1 hr, and the excess of acetic anhydride was then removed under reduced pressure. The product, the *lactol acetate* (0.16 g), was isolated as a colourless liquid, b.p. 115–120 °C/3 mm (Found: C, 68.6; H, 8.7%. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}_3$: C, 68.5; H, 8.6%). The product gave a yellow colour with tetranitromethane in chloroform solution.

(c) *Ozonolysis of the Lactol Acetate (VIIIb, VIIIc)*.—The lactol acetate (130 mg) was ozonized at 0 °C for 2 hr in dry carbon tetrachloride solution (50 ml) when a colourless gum slowly separated. The solvent was removed under reduced pressure at room temperature to yield a viscous product. A portion of this gum (10 mg) was decomposed with water (overnight) and then gave: (i) an immediate precipitate of iodoform with sodium hypiodite solution; (ii) a yellow precipitate with aqueous 2,4-dinitrophenylhydrazine sulphate solution; and (iii) a strong pyrrole pine splinter test (red) on fusion with ammonium acetate.

The remainder of the ozonide was decomposed in aqueous solution, but did not dissolve completely until oxidized with moist silver oxide (2 g) in sodium hydroxide solution (20 ml; 2N). This alkaline solution gave a copious precipitate of iodoform with sodium hypiodite solution. Portion of the solution, after acidification, and treatment with aqueous 2,4-dinitrophenylhydrazine

sulphate, precipitated yellow droplets of a keto acid 2,4-dinitrophenylhydrazone. It was extracted into benzene, then into sodium hydrogen carbonate solution, and reprecipitated as a yellow oil, on acidification. No crystalline compound could be isolated, even after chromatography on alumina.

(d) *Oxidation of Iridodial with Manganese Dioxide.*—Manganese dioxide, prepared by the method of Attenburrow *et al.* (1952), was washed with water to pH 9, then adjusted to pH 5 by the passage of carbon dioxide, dried at 105 °C (1 hr), and ground to a chocolate powder. The activity of the product was checked by the method of Weedon and Woods (1951). The active manganese dioxide (6 g), with freshly distilled iridodial (0.44 g), was shaken (48 hr) in light petroleum solution (40 ml). After removal of the excess manganese dioxide, and evaporation of the solvent, a viscous yellow oil (279 mg) remained. The oil in ether (20 ml) was treated with sodium hydrogen carbonate solution (5 ml), and after acidification with hydrochloric acid, the resultant organic acids (obtained by ether extraction) were isolated as a viscous yellow oil (134 mg), equiv. wt. 95.5. Neutralization with barium hydroxide solution gave an insoluble barium salt (45 mg), which was filtered off. The barium salt was further purified by conversion into the free acid, then reprecipitated. Nepetalinic acid (IIIa) was finally isolated by ether extraction, and obtained as colourless needles (17 mg), m.p. 83.5–84.5 °C, from light petroleum. The mixed m.p. with an authentic specimen was undepressed.

The filtrate of soluble barium salts gave a keto acid, isolated as the 2,4-dinitrophenylhydrazone. This product was not homogeneous. Paper chromatography of the 2,4-dinitrophenylhydrazone on Whatman No. 1 paper, employing as solvent ethanol–15*N* ammonia–water (80 : 5 : 15), gave two yellow spots, R_F 0.9 (keto acid 2,4-dinitrophenylhydrazone) and R_F 0.5 (unknown). The former spot accounts for approx. 90% of the product. The filtrate from the isolation of the above dinitrophenylhydrazones contained acid/s which could not be identified.

Neutral material (144 mg), from the original oxidation, was essentially unchanged iridodial, characterized as the bis-2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 223–224 °C.

(e) *Oxidation of Iridodial with Chromic Acid.*—(i) Chromic anhydride (5 g) was added in small portions over a period of $\frac{1}{2}$ hr to iridodial (2.5 g) in sulphuric acid (25 ml; 3*N*). A vigorous reaction occurred with each addition (70 °C), and considerable carbon dioxide was evolved. After 1 hr the resultant green solution (diluted with 200 ml water) was steam distilled.

The acidic distillate was treated with excess aqueous 2,4-dinitrophenylhydrazine sulphate solution, and the orange precipitate so formed filtered off. Resolution of this product, on alumina, gave acetaldehyde 2,4-dinitrophenylhydrazone, isolated as yellow needles (30 mg), m.p. and mixed m.p. 158–159 °C, from benzene–light petroleum (Found : N, 25.0%. Calc. for $C_8H_8O_4N_4$: N, 25.0%).

The residual distillate (including washings from the dinitrophenylhydrazone precipitation) was made alkaline (NaOH), evaporated to smaller bulk, then reacidified (sulphuric acid) and again steam distilled. The volatile acid fraction (150 mg) thus obtained was identified as acetic acid by conversion into the yellow 2-methylbenziminazole picrate, m.p. 208 °C (Found : N, 19.3%. Calc. for $C_{14}H_{11}O_5N_5$: N, 19.4%).

The residual green solution containing the non-volatile products was then extracted with ether (250 ml), and the colourless extract treated with an excess of sodium hydrogen carbonate solution. Only a trace of a neutral gum remained on evaporation of the dried ethereal layer. The acid fraction (650 mg) obtained after acidification (sulphuric acid) and re-extraction (ether), was shown by paper chromatography to contain two major components, one of which appeared to be a dibasic acid. Treatment of the mixture (600 mg) with an excess of 2,4-dinitrophenylhydrazine sulphate gave an orange precipitate (100 mg), which was filtered off. This product, difficultly crystallizable from aqueous ethanol, was finally obtained as golden plates (100 mg), m.p. 168 °C, from benzene (Found : C, 58.7; H, 5.6; N, 13.2%. Calc. for $C_{13}H_{13}O_4N_4$: C, 58.9; H, 5.6; N, 13.1%). The product lost benzene on crystallization on drying at 100 °C (reduced pressure) to give a nepetonic acid 2,4-dinitrophenylhydrazone, $[\alpha]_D^{20} \pm 0^\circ$ (c, 0.24 in $CHCl_3$, micro-cell), λ_{max} ($CHCl_3$) 365 m μ (Found : N, 16.2%. Calc. for $C_{13}H_{11}O_5N_4$: N, 16.0%).

Extraction of the residual solution (including the washings from the dinitrophenylhydrazone precipitation) with ether, yielded a viscous acidic oil (350 mg), b.p. 170–180 °C/0.5 mm. This

dibasic acid fraction, on treatment with aniline, gave an *N*-phenylimide, isolated as a viscous oil (20 mg) (Found: C, 74.5; H, 7.3; N, 5.2%. Calc. for $C_{16}H_{10}O_2N$: C, 74.7; H, 7.4; N, 5.4%).

(ii) Chromic anhydride (7.1 g) was added to iridodial (4.22 g) in sulphuric acid (50 ml; 4*N*) as described in (i). The evolved carbon dioxide was absorbed in barium hydroxide solution, and when the oxidation had ceased ($\frac{1}{2}$ hr), the mixture was refluxed ($\frac{1}{4}$ hr) to expel the remaining carbon dioxide (total barium carbonate, 1.14 g). A green solid separated from the reaction mixture.

The product was worked up in a manner similar to that described above. Volatile carbonyl compounds, isolated as a mixture of 2,4-dinitrophenylhydrazones, were obtained as a yellow oil (230 mg). Acetic acid was isolated as the *p*-bromophenacyl ester (33 mg), m.p. and mixed m.p. 85 °C. The same nepetonic acid 2,4-dinitrophenylhydrazone (27 mg) was obtained as golden plates, m.p. 168 °C, from benzene. The m.p. was undepressed on admixture with the product isolated in (i).

The residual green solution (from the original steam distillation) was then filtered, giving a green chromium complex (590 mg), insoluble in 10*N* hydrochloric acid and in ether, but swollen by aqueous ethanol. The chromium complex, on oxidation with hydrogen peroxide (1 ml; 30%) in sodium hydroxide solution (10 ml; *N*), liberated chromate, whence acidification of the solution, then extraction with ether, gave a viscous acidic gum (226 mg). This acidic product gave a positive iodoform test, but no reaction with 2,4-dinitrophenylhydrazine sulphate solution.

The residual green solution was extracted with ether, and the ethereal layer washed with sodium hydrogen carbonate solution. The viscous neutral product (532 mg) isolated from the ethereal layer contained much unchanged iridodial. Acidification, then ether extraction, of the alkaline layer gave an acidic product (1.415 g), having the same qualitative tests as the acids (226 mg) obtained from the chromium complex.

The combined acids (1.305 g) were esterified with methanol, in the presence of dry hydrogen chloride, yielding a pleasant smelling product (1.19 g), which still gave a positive iodoform test, but no reaction with 2,4-dinitrophenylhydrazine sulphate solution. The methyl esters were distilled under reduced pressure to yield a colourless liquid (664 mg), b.p. 85–90 °C/0.8 mm, $[\alpha]_D^{20} +5.0^\circ$ (c, 4.01 in 95% ethanol), equiv. wt. 150.3. Paper chromatography of the acids (from these esters) suggested a mixture of monobasic, and a majority of dibasic acids. The infra-red absorption spectrum (carbon disulphide) of the methyl esters showed a strong band at 1785 cm^{-1} , indicative of a γ -lactone. This band was reduced by 95% on reaction of the esters with excess alkaline sodium hypoiodite solution. Iodoform (70 mg) was isolated as hexagonal plates, being purified by sublimation.

A carbon balance is given below, and the loss may be ascribed to soluble chromium complexes remaining in the green oxidation liquors.

Carbon Balance					g-Atom of Carbon
BaCO ₃ (1.14 g)	0.006
Volatile keto acid DNP	0.001
Acetic acid	0.020
Volatile neutral (as iridodial)	0.005
Non-volatile neutral (as iridodial)	0.031
Non-volatile acids (as $C_{10}H_{16}O_4$)	0.080
Chromium complex acids	0.030
					0.173
Iridodial ($C_{10}H_{16}O_2$ 4.216 g)	0.251
Loss	0.078

(f) *Derivatives of α -(2-Oxo-3-methylcyclopentyl)propionic Acid.*—(i) α -(2-Oxo-3-methylcyclopentyl)propionic acid (50 mg), prepared according to the method of Jones and Linstead (1936), was heated with phenylhydrazine (100 mg) at 100 °C ($\frac{1}{2}$ hr), forming a colourless gum, which was

trituted with benzene (2 ml), and hydrochloric acid (5 ml; 2N). The *1',4-dimethyl-2-phenyl-5,6-cyclopentano-3[2H]-pyridazone* (45 mg) was filtered off and isolated as colourless rhombs, opaque at 125–128°C, m.p. 198.5°C, from benzene (Found: C, 77.4; H, 6.7; N, 10.5%. Calc. for $C_{15}H_{18}ON_2 \cdot \frac{1}{2}C_6H_6$: C, 76.9; H, 7.5; N, 10.0%). The product is insoluble in dilute sodium hydroxide solution. Benzene of crystallization was removed on drying the product at 140°C ($\frac{1}{2}$ hr) (Loss on drying: 13.6%. Calc. for $C_{15}H_{18}ON_2 \cdot \frac{1}{2}C_6H_6$: 13.9%). The solvent-free pyridazone was finally isolated as colourless leaflets, m.p. 200°C, from ethanol. The infra-red spectrum contained no NH or OH bands in the 3 μ region.

(ii) The keto acid (520 mg) in iced water (200 ml) was treated with 2,4-dinitrophenylhydrazine (640 mg) in sulphuric acid (60 ml; 50%). The resultant yellow precipitate was filtered off, washed, and dried. α -(2-Oxo-3-methylcyclopentyl)propionic acid 2,4-dinitrophenylhydrazone was obtained as yellow needles, m.p. 226°C (decomp.), from ethanol (Found: C, 51.5; H, 5.0; N, 15.8%. Calc. for $C_{15}H_{18}O_8N_4$: C, 51.4; H, 5.2; N, 16.0%). The product forms a yellow solution at pH 7, and a purple-red solution at pH 11, in 2N sodium hydroxide. It is reprecipitated on acidification.

(g) *Reaction of Iridodial with Alkali.*—(i) *Lactonization of the Water-Insoluble δ -Hydroxy Acid (XVII).* Freshly distilled iridodial (2.98 g) was refluxed (2 hr) in 90% ethanolic N potassium hydroxide solution, and the alcohol was then removed. Extraction with ether gave a neutral fraction (261 mg). Titration with hydrochloric acid showed the reaction of 1.04 moles of potassium hydroxide per mole of iridodial. Adjustment to pH 5 then precipitated the colourless δ -hydroxy acid (XVII) (1.40 g), m.p. 106–107°C, which was recrystallized as colourless needles, m.p. 127°C, from aqueous ethanol (Found: C, 64.6; H, 9.5%. Calc. for $C_{16}H_{18}O_3$: C, 64.5; H, 9.7%). The δ -hydroxy acid is very sparingly soluble in water, thus allowing its separation from other δ -hydroxy acids.

The hydroxy acid (196 mg) gave isoiridomyrmecin [lactone fraction (1)] (178 mg), m.p. and mixed m.p. 58–59°C, $[\alpha]_D^{19}$ —64° (c, 1.0 in CCl_4), on sublimation at 120°C/0.2 mm; that is, in 100% yield (cf. Parts I and II, loc. cit.).

(ii) *Fractional Lactonization of the Water-Soluble δ -Hydroxy Acids.* The aqueous solution (pH 5) of the soluble δ -hydroxy acids, which remained after filtration of XVII, was neutralized with sodium hydrogen carbonate solution, then extracted with ether to give a mixture of lactones. These are lactone fractions (2) and (3), and they contain lactonizable acids (544 mg). Separation into readily (2), and fairly readily (3), lactonizable acids was achieved by hydrolysis with 2N sodium hydroxide solution (5 ml), the mixture being heated on the steam-bath (15 min). Acidification to pH 5, followed by addition of excess sodium hydrogen carbonate solution, then ether extraction (5 \times 20 ml), yielded the readily lactonizable acids as fraction (2), a colourless oil (128 mg), $[\alpha]_D^{15} +4.1^\circ$ (c, 1.26 in $CHCl_3$). The fairly readily lactonizable acids were obtained from the aqueous residue after acidification with an excess of hydrochloric acid. Ether extraction (5 \times 20 ml) gave lactone fraction (3), as a colourless oil (280 mg).

The acidic aqueous residues were then further extracted with ether (5 \times 50 ml) to yield a mixture of oily acids (846 mg), equiv. wt. 195 [calc. for the hydroxy acid ($C_{16}H_{18}O_3$), 186]. These acids gave soluble lead salts and only a trace of an insoluble barium salt. This mixture of difficultly lactonizable acids yielded lactone fraction (4) (446 mg), $[\alpha]_D^{20} +12.7^\circ$ (c, 4.46 in $CHCl_3$), on sublimation at 120–140°C/0.3 mm. The residue gave a trace of the insoluble barium salt of nepetalinic acid (IIIa).

(h) *Oxidation of the Lactone Fractions with Potassium Permanganate.*—(i) *isoiridomyrmecin* (lactone fraction (1)) was converted into the nepetalinic acid (IIIa) as previously described (Cavill and Locksley 1957). This acid (80 mg), m.p. 85°C, was neutralized with 2N sodium hydroxide solution (phenolphthalein), evaporated to dryness (steam-bath), then refluxed in ethanol (2 ml) with *p*-bromophenacyl bromide (240 mg) for 2 hr. On cooling and standing, the ester (90 mg), m.p. 70°C, slowly separated. *Nepetalinic acid (IIIa) di-p-bromophenacyl ester* was finally obtained as colourless needles, m.p. 71–72°C, $[\alpha]_D^{20} -109^\circ$ (c, 2.63 $CHCl_3$, microcell), from ethanol (Found: C, 52.6; H, 4.4%. Calc. for $C_{22}H_{26}O_6Br_2$: C, 52.5; H, 4.4%).

(ii) The following procedure was used for the oxidation of the remaining lactone fractions: The lactone fraction (1 part) was dissolved in a solution of potassium hydroxide (1.2 parts) in

water (18 parts) at room temperature, then treated with potassium permanganate (2.4 parts) in water (40 parts) at 0 °C (2 hr). The reaction mixture was allowed to stand at room temperature (2 days) when the permanganate colour had disappeared, and manganese dioxide had precipitated. The manganese dioxide was filtered off, washed with water (3 × 2 ml), and the combined filtrates acidified with dilute hydrochloric acid. The mixture of dicarboxylic acids was then isolated by ether extraction (6 × 10 ml).

Lactone fraction (2) (128 mg) gave a mixture of colourless acids as a gum (124 mg), equiv. wt. 99 [calc. for the dicarboxylic acid ($C_{10}H_{16}O_4$), 100]. Treatment with barium hydroxide solution gave an insoluble salt (162 mg). [The soluble barium salts yielded a mixture of gummy acids (26 mg), which was not investigated.] The insoluble salt was decomposed with hydrochloric acid (10 ml; 2N) and the product extracted into ether (5 × 5 ml); removal of the solvent gave a crystalline solid (90 mg). Fractional crystallization from benzene yielded *cis*-nepetic acid (10 mg), m.p. 132 °C identical with an authentic specimen. Fractional crystallization of the benzene soluble acids, from light petroleum, gave nepetalinic acid (IIIa) (46 mg), m.p. and mixed m.p. 84–85 °C. This acid must be derived from a dihydronepetalactone (type XIX).

(iii) Lactone fraction (3) (230 mg) gave a mixture of colourless acids as a gum (233 mg), equiv. wt. 93.4. These acids were separated into gummy acids (117 mg) with soluble barium salts, not further investigated, and the nepetalinic acid (IIIa) (102 mg) which was isolated as the insoluble barium salt (231 mg). Nepetalinic acid (IIIa) was recrystallized as colourless prisms (73 mg), m.p. and mixed m.p. 84–84.5 °C, from light petroleum. Fraction (3) also contains the dihydronepetalactone.

(iv) Lactone fraction (4) yielded a mixture of colourless acids (355 mg), equiv. wt. 119, which solidified on cooling. The mixture gave no reaction with 2,4-dinitrophenylhydrazine sulphate, no iodoform reaction, and no insoluble barium salt/s.

An extensive fractional crystallization from water, and then from light petroleum (16 crystallization stages with attendant recombinations), ultimately gave three products.

(1) *Nepetalinic acid* (IIIc) (73 mg), m.p. 132 °C, $[\alpha]_D^{23} + 27^\circ$ (c. 0.94 in $CHCl_3$, microcell), $[\alpha]_D^{26} - 7.1$ (c. 0.79 in 95% ethanol, microcell), equiv. wt. 101 (calc. 100) (Found: C, 60.3; H, 7.9%. Calc. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1%). This acid is dimorphous, crystallizing from a melt with m.p. 118 °C, then solidifying, m.p. 132 °C.

The *di-p-bromophenacyl ester*, obtained as above, has m.p. 134 °C, $[\alpha]_D^{20} + 6.7^\circ$ (c. 1.33 in $CHCl_3$, microcell).

(2) *Nepetalinic acid* (IIIb) (95 mg), m.p. 113–114 °C. The mixed m.p. with an authentic specimen (m.p. 114–115 °C) was 113–114 °C, $[\alpha]_D^{20} + 13.2^\circ$ (c. 0.82 in $CHCl_3$, microcell), equiv. wt. 102 (Found: C, 60.3; H, 8.0%).

This acid (IIIb) (5 mg) was converted into its *di-p-bromophenacyl ester*,* obtained as colourless needles, m.p. 127–127.5 °C, $[\alpha]_D^{20} + 13.6^\circ$ (c. 1.76 in $CHCl_3$, microcell) (Found: C, 52.1; H, 4.5%).

(3) The mother liquors from the isolation of the above acids gave a pasty mixture (100 mg) which could not be resolved.

(j) *Nepetalinic Acid* (IIIId).—Iridodial (2.90 g) was reacted with potassium hydroxide [3 g in 50% ethanol (100 ml)] at 100 °C for 5 hr, and the mixture of δ -hydroxy acids, which resulted, was separated into lactone fractions as described in (g). Oxidation of each lactone fraction with

* This ester is identical with the major constituent isolated from the mixed acids, obtained by direct oxidation of iridodial with potassium permanganate (see Part I). The original specimen had m.p. 125–125.5 °C, $[\alpha]_D^{18} - 15^\circ$ (c. 1.12 in $CHCl_3$), but on repeated recrystallization from ethanol, then light petroleum, it has m.p. 124–126 °C, $[\alpha]_D^{20} + 12.6^\circ$ (c. 0.333 in $CHCl_3$, microcell). The minor constituent is probably the ester of acid (IIIa) (cf. Table 1). Whereas the melting points of the various nepetalinic acids show a 20 °C depression on admixture (McElvain and Eisenbraun 1955), such mixed m.p. determinations are inconclusive for their *di-p-bromophenacyl esters*.

potassium permanganate solution, as described in (h), gives the products already reported above, and in addition, fraction (3) yields a new acid. The oxidation of lactone fraction (3) (268 mg) gives a mixture of colourless dicarboxylic acids (166 mg), which partly solidified on standing. Extensive fractional crystallization from water, then light petroleum, yields nepetalinic acid (IIIc) (4 mg), m.p. 130–131 °C. Mixed m.p. with the specimen isolated in (h) (iv) is 131–132 °C. Then nepetalinic acid (IIIId) is obtained as colourless prisms (15 mg), m.p. 120–120.5 °C, $[\alpha]_D^{20} +36.2^\circ$ (c, 2.02 in CHCl_3 , microcell).

(k) *Epimerization of Nepetalinic Acid (IIIc)*.—An ethereal solution of pure diazomethane was slowly added to nepetalinic acid (IIIc) (5 mg), m.p. 132 °C, in dry ether (0.1 ml), until a faint yellow colour persisted. Nitrogen was evolved. Removal of the solvent gave the dimethyl ester as a colourless oil, which was then heated at 100 °C (2 days) in a sealed tube with sodium methoxide solution (5 mg sodium in 0.5 ml dry methanol). The product was saponified, excess methanol was removed, and the resultant acids isolated by extraction of the acidified solution with ether (6 × 0.2 ml). Fractional crystallization of the product (5 mg) from water gave the nepetalinic acid (IIIId) (2 mg), m.p. 119–120.5 °C. Mixed m.p., with the specimen isolated in (j), was 119–120 °C.

VIII. ACKNOWLEDGMENTS

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SHORT COMMUNICATIONS

A PROPOSED NEW METHOD FOR THE DETERMINATION OF THE TEMPERATURE VARIATION OF VIRIAL COEFFICIENTS*

By G. A. BOTTOMLEY†

High precision virial coefficients of vapours, preferably over a wide temperature range and in the absence of mercury vapour, are needed for comparison with values computed from intermolecular potentials. In this note attention is drawn to a novel experimental method which offers distinct advantages over techniques so far exploited.

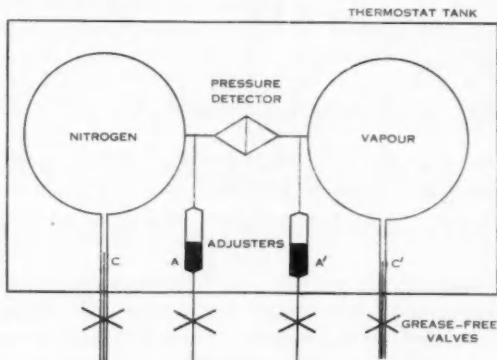


Fig. 1.—General arrangement of apparatus suitable for new method.

The basic scheme is indicated in Figure 1. Samples of nitrogen (provisionally regarded as a perfect gas) and the experimental vapour are confined in the two halves of the symmetrical apparatus and adjusted to the same pressure as indicated by a null-point pressure-sensing device. The temperature is changed substantially and the pressure equality restored by the use of the volume adjuster A' only.

At subatmospheric pressures the equation of state can be taken to be

$$PV = nRT + nBP,$$

which rearranges to

$$B = \frac{V}{n} - \frac{RT}{P}.$$

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If the pressure balance is performed at T_1 and T_2 then, for the vapour,

$$B_1 - B_2 = \frac{V_1}{n} - \frac{V_2}{n} - \frac{RT_1}{P_1} + \frac{RT_2}{P_2}.$$

But the last two terms are equal since the pressure of the vapour on each occasion was equal to that of the ideal gas whose pressure is proportional to the absolute temperature. Hence the remarkable result that

$$B_1 - B_2 = \frac{\Delta V}{n}, \dots\dots\dots (1)$$

so that B as a function of T can be obtained from one standard value, the measured volume changes, and the molar quantity of vapour.

When the expansion in terms of $1/V$ is preferred one can start from

$$\frac{PV}{nRT} = 1 + \frac{nB^*}{V},$$

and similarly deduce

$$\begin{aligned} B_1^* - B_2^* &= \frac{V_1^2 - V_2^2}{n^2 RT/P} - \frac{V_1 - V_2}{n} \\ &= \frac{\Delta V(2V_1 - \Delta V)}{n^2 RT/P} - \frac{\Delta V}{n}. \dots\dots\dots (2) \end{aligned}$$

Note that $(2V_1 - \Delta V)/(nRT/P)$ is close to 2, so the second term is about half the first.

It is to be especially noted that a small volume change is measured, not—as in most other methods—two closely similar large PV values which are then differenced with striking loss of precision. There is no need for precision pressure measurements, merely a pressure balancing. Temperature measurement to 0.1°C suffices, although the thermostat should hold the temperature constant to within 0.003°C .

It is instructive to substitute numerical values into the basic equations (1) or (2). Consider an apparatus with capacities of 1 l., at pressures of about 500 mm, that is, 0.025 mole. There is no difficulty in admitting this quantity of vapour, known to 1 in 1000 or better, either by gravimetric methods or by volumetric methods plus an assumed preliminary value of B . With a temperature increase of 100°C the virial coefficient will commonly change by 200 c.c./mole or more. The volume change will accordingly be 5 c.c. If the pressure-sensing device is sensitive to 0.005 mm the volume adjuster can be positioned to 0.01 c.c., giving an accuracy in ΔB of better than 1 c.c./mole.

By loading the apparatus to different initial filling pressures two implicit assumptions in the elementary theory can be tested for if either higher virial coefficients or adsorption effects are significant then $\Delta V/n$ and ΔB will vary with the filling pressure. Corrections for the non-ideality of the nitrogen can be applied using standard isotherm data and a slightly more complex theory.

Rough estimations indicate that the varying adsorption on the walls due to rising pressure and temperature during an experiment might produce errors of the order of 1 c.c./mole with litre vessels. Adsorption is a limiting problem in other types of PV apparatus. Doubling the size of the vessels, in the present design an easy change, reduces the error to one-half.

In this preliminary paper it is not necessary to recommend detailed procedures* but some comments on practical points are warranted. The symmetrical design of the apparatus eliminates errors due to thermal expansion of the apparatus and pressure dilation. Suitable corrections will be required for the density change of the volume adjuster working substance. With a liquid manometer as pressure-sensing device it will be necessary to measure the co-volume over the meniscus surface at every pressure setting. The apparatus makes minimum demands on the amount of confining fluid for the gases as it is never necessary to compress the gases substantially by transfer of liquid as in a Boyle-type apparatus. Liquid metal surfaces are only required at A, A', C, C' , and possibly in the pressure-sensing device: thus the arrangement is very suitable for use with the expensive gallium as working fluid. With gallium or tin and silica vessels, experiments might conveniently be performed over very long temperature ranges. The basic idea is also applicable to above-atmospheric pressures though at high non-idealities a relatively large volume adjuster is required.

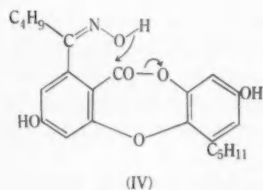
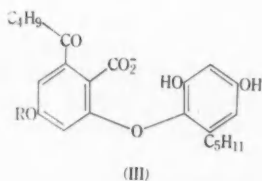
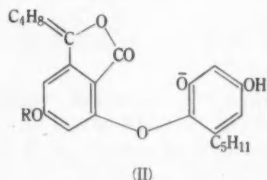
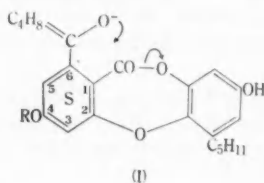
Finally, one important variation may be mentioned. One half of the apparatus can be made *wholly* of glass or silica when a distortion type gauge is used as detector so permitting the examination of the PV behaviour of mercury vapour or substances corrosive to metals.

* Much relevant information on the precision manipulation of gases and vapours can be found in the more recent papers of the late Professor R. Whytlaw-Gray and his collaborators.

REACTION MECHANISMS OF CERTAIN 2,6-DISUBSTITUTED BENZOIC ACID DERIVATIVES*

By G. E. GREAM† and N. V. RIGGS‡

Steric effects in 2,6-disubstituted benzoic acids are most clearly discerned in acid-catalyzed esterification (mechanism A_{Ac} 2) rates of which are not sensitive to polar influences (Ingold 1953 ; Taft in Newman 1956, Ch. 13). If one of the *ortho*-substituents is attached by a carbonyl group steric hindrance to esterification may not be observed, a pseudo-ester often but not necessarily being formed (Newman and Muth 1951). Formation of pseudo-ester may occur via a hemiketal (Newman and McCleary 1941), or it may be a reaction of the lactol form of the acid, neither presenting a typical example of mechanism A_{Ac} 2. Similarly, although esters of 2,6-disubstituted benzoic acids are subject to steric hindrance to fission by the normal B_{Ac} 2 mechanism, fission of a suitably constituted ester in alkaline solution may follow some other path.



Norlobaridone (Gream and Riggs 1960) gives no evidence of steric hindrance to fission of the ester linkage in being very rapidly isomerized by cold 1N sodium hydroxide to isonorlobaridone. The same product results with warm sodium carbonate or hot sodium acetate solution. The structure of the product coupled with its slow and probably irreversible hydration in alkaline solution to norlobarilol shows that the isomerization does not proceed through attack by external base on the ester carbonyl group. Instead the mesomeric enolate ion (I ; R = H)§

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§ In these structures I-IV ionized groups other than those immediately involved in reaction are not shown ; ionization of phenolic groups undoubtedly occurs in the alkaline media.

produced by abstraction of a proton by base undergoes rapid internal reaction (arrows) to produce the phenoxide ion (II; $R=H$) corresponding to *isonorlobaridone*. Similar processes probably occur in the rapid conversion of a number of depsides or depsidones with β -ketoalkyl substituents in position 6 of ring 8 into δ -enol lactones by cold dilute sodium hydroxide (e.g. physodic acid into *isophysodic acid*; Asahina and Nogami 1934). It seems likely that the original depside or depsidone carbonyl carbon atoms become tetrahedral in the transition states for the isomerizations for which the mechanism may be described as an internal variety of mechanism $B_{Ac} 2$, but it is not clear how far this bears on the geometry of the transition state for the normal $B_{Ac} 2$ mechanism. A tetrahedral intermediate as in normal $A_{Ac} 2$ or $B_{Ac} 2$ reactions (Bender 1951) may also be formed.*

The carbonyl group in II ($R=H$) is not seriously hindered to attack by external reagents, but hydration to norlobariol in alkaline solution probably occurs through attack of hydroxide ion on the cyclic enolic carbon atom followed by proton transfer and lactol ring opening to give the *o*-ketocarboxylate ion (III; $R=H$) (cf. ultraviolet absorption spectrum of dimethyl-lobariol in alkaline solution; Gream and Riggs 1960). Such a view is supported by the conversion of *isonorlobaridone* into lobariol methyl pseudo-ester by methoxide ion in methanol; in this case, proton transfer is not possible and the initial product is stabilized by attachment of a proton at the side-chain carbon atom adjacent to the ketol carbon atom.

Even brief treatment of lobaric acid with cold alkali opened the depsidone ring with addition of the elements of water to give lobariolcarboxylic acid; more vigorous treatment caused decarboxylation to lobariol (Asahina and Nonomura 1935). The action of bases on lobaridone has therefore been examined under conditions in which norlobaridone gives good yields of the isomeric enol-lactone, but the only crystalline product obtained was lobariol. Direct attack of hydroxide ion on the ester carbonyl group may here occur but the speed of the reaction gives no indication of steric hindrance and it seems more likely that an intermediate (II; $R=Me$) is produced in the same way as intermediate II ($R=H$) from norlobaridone, and rapidly hydrated as above to the *o*-ketocarboxylate ion (III; $R=Me$). The much lower rate of hydration of II ($R=H$) is then accounted for by the negative charge on ring 8 arising from ionization of the relatively acidic hydroxyl group OR. Such a factor does not however account for the isolation of lobariol by Asahina and Nonomura (1935) from the action of boiling formic acid on lobaric acid.

The depsidone ester linkage in norlobaridone is readily broken by hydroxylamine in aqueous ethanolic sodium acetate or pyridine solution. Under these conditions *isonorlobaridone* yields the same product, norlobariol oxime anhydride, presumably by attack of hydroxylamine (or a conjugate base) on the cyclic enolic

* Bender (1951) claimed that a *symmetrical* intermediate was required by his results. The intermediate has been assumed to be tetrahedral (e.g. Newman 1956). The argument of Dewar (1949) for a planar transition state in mechanism $B_{Ac} 2$, modified to allow for occurrence of the intermediate, suggests an appreciably flattened tetrahedral transition state (see also Day and Ingold 1941; Ingold 1953).

carbon atom followed by appropriate proton transfers and ring opening and closure. Norlobaridone is stable to boiling pyridine, alone or in the presence of ammonium chloride, and its conversion into norlobarior oxime anhydride in this solvent is probably an internal reaction (arrows) of the oxime (IV) formed initially or of its anion. The same pathway may be followed in the reaction in aqueous ethanol, or isonorlobaridone may be an intermediate. It is interesting that whereas norlobarior methyl pseudo-ester does not react with hydroxylamine in aqueous ethanolic sodium acetate (cf. Langlois and Wolff 1948; Grove and Willis 1951) norlobarior oxime anhydride is produced in pyridine solution. Hydroxylamine hydrochloride is likely to form a reasonably strongly acidic solution in pyridine and we interpret the reaction in this medium to be due to protonation of the acetal-like methoxyl group followed by reaction with hydroxylamine in an S_N1 process (Ingold 1953), or possibly an S_N2 process in the present poorly ionizing solvent.

Experimental

Some results have been given previously (Gream and Riggs 1960). Products below were isolated and purified as there described, and identified by m.p. and mixed m.p. determinations with authentic samples.

(a) *Reactions of Norlobaridone*.—(i) Norlobaridone (200 mg) dissolved rapidly in 1N sodium hydroxide (10 ml) at room temperature. After 1 min acidification with 2N hydrochloric acid (10 ml) gave isonorlobaridone (180 mg, 90%). With 2N sodium hydroxide acidification after 10 min gave isonorlobaridone (65%) and from the mother liquors was isolated norlobarior (c. 20%). After 85 hr the product was norlobarior (85%).

(ii) Norlobaridone (300 mg) was heated on the water-bath with 10% sodium carbonate solution (50 ml) until it had dissolved (10 min). Cooling and acidification gave isonorlobaridone (190 mg).

(iii) A mixture of norlobaridone (400 mg) in ethanol (5 ml) and crystalline sodium acetate (2.50 g) in water (5 ml) was refluxed for 2 hr. Addition of water and recrystallization gave isonorlobaridone (300 mg).

(iv) Norlobaridone (200 mg) was refluxed in pyridine solution (5 ml) for 3 hr with or without addition of ammonium chloride (400 mg). Starting material (180 mg) was recovered in each case.

(b) *Reactions of isoNorlobaridone*.—(i) isoNorlobaridone was refluxed with 1N sodium hydroxide for 1 hr. Acidification and recrystallization gave norlobarior (90%).

(ii) Treatment of isonorlobaridone with 2N sodium methoxide in methanol at room temperature for 2 hr, acidification with glacial acetic acid, evaporation, and recrystallization gave norlobarior methyl pseudo-ester (85%).

(iii) A mixture of isonorlobaridone (200 mg), hydroxylamine hydrochloride (400 mg), and crystalline sodium acetate (1.00 g) was refluxed in 50% aqueous ethanol (5 ml) for 3 hr. Addition of water and recrystallization gave norlobarior oxime anhydride (165 mg).

(iv) Refluxed with twice its weight of hydroxylamine hydrochloride in pyridine solution for 3 hr, isonorlobaridone gave norlobarior oxime anhydride (80%).

(c) *Reactions of Lobaridone*.—(i) Lobaridone (100 mg) was shaken with 2N sodium hydroxide (5 ml) at room temperature. The solid dissolved only slowly and, after 3 min, the mixture was filtered, the washed and dried residue (26 mg) being starting material. After a further 1 min the filtrate was acidified and gave lobarior (58 mg).

(ii) Lobaridone (111 mg) was heated on the water-bath with 10% sodium carbonate solution (50 ml) for 10 min. Cooling and acidification gave lobarior (65 mg).

(iii) A mixture of lobaridone (110 mg) in ethanol (2 ml) and crystalline sodium acetate (500 mg) in water (1 ml) was refluxed for 2 hr. The cooled mixture was poured onto crushed ice to give an oil that slowly solidified, but the product could not be crystallized from a variety of solvents tried.

(d) *Reaction of Norlobariol Methyl Pseudo-Ester with Hydroxylamine.*—After being refluxed with hydroxylamine hydrochloride and sodium acetate in 50% aqueous ethanol solution for 3 hr, norlobariol methyl pseudo-ester was recovered in 90% yield. Refluxing with hydroxylamine hydrochloride in pyridine however gave norlobariol oxime anhydride (c. 60%), and pseudo-ester (c. 20%) was recovered from the mother liquors.

This work was carried out during the tenure of a C.S.I.R.O. Senior Post-Graduate Studentship by one of us (G.E.G.).

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THE *para*:*ortho* RATIO IN THE MONOCHLORINATION OF PHENOL*

By G. H. BING,[†] W. W. KENNARD,[†] and D. N. MATTHEWS[†]

Holleman and Rinkes (1911) reported that only *p*- and *o*-chlorophenol were obtained when an equimolar amount of chlorine was passed into molten phenol and quoted a *para*:*ortho* ratio of approximately 1:1, which was only slightly influenced by temperature. Fierz David and Blangey (1949) stated: "The action of free chlorine on phenol is so vigorous that trichlorophenol is formed at once." Holleman's work is still quoted in many of the recent books on theoretical chemistry (e.g. De la Mare and Ridd 1959).

In view of the importance of the *para*:*ortho* ratio in reaction mechanisms, we wish to correct the figures given by Holleman and Rinkes (*loc. cit.*) and report work carried out in this laboratory during 1953 when we were interested in the production of *p*-chlorophenol.

Varying figures for the melting point of *p*-chlorophenol have been reported. For example 37 °C is given by Peratoner (1898) whilst Puschin and Dimitrijević (1939) found that *p*-chlorophenol exists in two modifications melting at 34 and 43 °C respectively. This fact is not recorded by Huntress (1948).

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The Monochlorination of Phenol

Preliminary experiments by Dr. C. M. Gibian and Mr. J. E. Oliff of this laboratory (unpublished data) confirmed Holleman's work in so far that no caustic insoluble or unexpected by-products were formed when chlorine was passed into molten phenol at 60 °C. A balance between hydrochloric acid evolved and chlorophenols formed was obtained and it was shown that 2,4- and 2,6-dichlorophenols (both identified as the corresponding dichlorophenoxy-acetic acids) were formed even while considerable quantities of unreacted phenol were still present.

Accordingly a stage of chlorination was selected in this work where the amount of monochlorophenols was substantial but the conversion to dichlorophenols was less than 3 per cent. Thus correction to the *para*:*ortho* initial ratio due to further chlorination of the monochlorophenols was small.

Experimental

Molten synthetic phenol (400 gal; crystallizing point 40.7 °C) was chlorinated at about 60 °C to a density of 1.22/20 °C. The material was freed of dissolved HCl gas by air-blowing, until less than 0.05% HCl remained. A sample of this product was fractionated *in vacuo* through a 3 ft by 1 in. glass column packed with $\frac{1}{8}$ in. cylindrical stainless-steel gauze rings, using a reflux ratio of 30:1. Although little decomposition occurred, the last part of the charge after fraction 9, was distilled, bypassing the column. Table 1 presents the results.

TABLE 1
EXPERIMENTAL RESULTS

Fract. No.	Boiling Range/52 mm (°C)	d_{20} Calc. as Liquid*	Crystallizing Point (°C)†	Wt. (g)	Composition (g)				
					2-Chloro-phenol	Phenol	2,4-Di-chloro-phenol	4-Chloro-phenol	2,6-Di-chloro-phenol
1	92-93	1.262	9.0	157	157	—	—	—	—
2	93-103.5	1.159	—	31	16	15	—	—	—
3	103-104	—	40.3	139	1	138	—	—	—
4	104-128.5	1.184	15-16	27	—	16	8	3	—
5	128.5-130.5	1.311	—	13	—	—	3	10	—
6	130.5-132	1.290	37.5	23	—	—	2	21	—
7	132-132.5	1.290	38.3	18	—	—	1½	16½	—
8	132.5	—	42.9	33	—	—	—	33	—
9	132.5-132.8	1.284	43.25	51	—	—	—	51	—
10	120-144/30mm	1.289	42.6	153	—	—	—	151	2
11	—	—	40.6	10	—	—	—	9½	½
Residue	—	—	—	7	—	—	—	6½	½
Total (g)	662	174	169	14½	301½	3
Total (% wt.)	100	26.3	25.5	2.2	45.5	0.5

* Densities were measured in the molten state and corrected to 20 °C, using a correction factor of 0.001 per degree.

† Crystallizing point determination: Molten samples were cooled in a 1 by 6 in. test tube fitted with glass ring stirrer and thermometer. The crystallizing point was taken as the point where the temperature remained approximately constant.

Physical Data: (i) Basis of Analysis of Fractions

Fraction 1: Pure 2-chlorophenol from density and boiling point.

Fraction 2: From boiling range considered as mixture of phenol and 2-chlorophenol. Synthetic blends of these were prepared to match the density of the sample.

Fraction 3: From boiling point considered as mixture of phenol and a little 2-chlorophenol. Analysed by freezing point depression.

Fraction 4: From boiling range considered as mixture of phenol, 2,4-dichlorophenol and 4-chlorophenol. Synthetic blends were prepared to match density and crystallizing point of the sample.

Fraction 5: From boiling range considered as mixture of 2,4-dichlorophenol and 4-chlorophenol; analysed by density.

Fractions 6 and 7: From boiling range considered as mixture of 2,4-dichlorophenol and 4-chlorophenol. Analysed by freezing point depression.

Fraction 8: Approx. pure 4-chlorophenol from crystallizing point.

Fraction 9: Pure 4-chlorophenol from crystallizing point.

Fractions 10 and 11: From boiling range considered as mixture of 4-chlorophenol and 2,6-dichlorophenol. Analysed by freezing point depression.

Residue: Assumed to consist of 4-chlorophenol and 2,6-dichlorophenol; 4-chlorophenol content calculated by extrapolation of the composition of the two preceding fractions.

Since the analyses depend on fractional distillation it is important to know that no azeotropes are formed between the compounds constituting the sample. No reference was found in the literature nor was evidence found in this work that such azeotropic mixtures form.

(ii) Some Physical Data used in the Analysis

The physical data used in the analysis are presented in Table 2.

TABLE 2
PHYSICAL DATA IN THE ANALYSIS

Compound	d_{20}	Crystallizing Point (°C)	B.P./52 mm* (°C)	References
2-Chlorophenol	1.262	9.0	89	d_{20} and crystallizing point from this report; m.p. 8.7 °C (Holleman and Rinkes loc. cit.); $d_{25}=1.2573$ (Anziletti and Curran 1943); cryoscopic constant 77.2 (Jona 1909)
Phenol	1.080	41.0	105	Personal communications
2,4-Dichlorophenol	1.420	42.8	130	From reports of this laboratory (Gibian and Richardson, unpublished data)
4-Chlorophenol	1.284	43.25	132	Cryoscopic constant 85.8 (Jona loc. cit.); d_{20} and crystallizing point from this paper; sp. gr. $78.1/4=1.2238$ (von Auwers 1932)
2,6-Dichlorophenol	—	—	138	

* Calculated from Perry, J. H. (1950).—"Chemical Engineering Handbook." 3rd Ed. p. 153 ff. (McGraw-Hill Book Co.: New York.)

During this work it was found that *para*-monochlorophenol would crystallize occasionally in opaque fine needles of crystallizing point 34.7°C instead of the stable high melting transparent form crystallizing point 43.3°C . This confirms work by Puschin and Dimitrijević (loc. cit.).

Calculation of Para : Ortho Ratio

To calculate the *para* : *ortho* ratio a small correction must be made for the dichlorophenols formed. The 2.7 per cent. of total dichlorophenols found have been formed from 2.1 per cent. of 2- and 4-chlorophenols. From other information (unpublished data) we have calculated that 1.1 per cent. of 4-isomer was converted to 2,4-dichlorophenol and 1.0 per cent. of 2-isomer was converted to 2,4- and 2,6-dichlorophenols. Derived monochlorophenol percentage content is therefore :

$$\text{4-isomer : } 45.1 + 1.1 = 46.6$$

$$\text{2-isomer : } 26.3 + 1.0 = 27.3$$

$$\text{para : ortho ratio : } 1.7 : 1$$

This ratio has been subsequently confirmed in this laboratory by infra-red analysis.

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REACTIONS OF ALKOXY RADICALS

II. THERMAL DECOMPOSITION OF *n*-OCTYL NITRITE IN *n*-BUTYRIC ACID*

By A. L. J. BECKWITH†

The reaction of di-*tert*.-butyl peroxide with *n*-butyric acid has been shown (Beckwith 1960) to proceed by abstraction of hydrogen from the α -position thus indicating that *tert*.-butoxy radicals are not strongly electrophilic and that resonance stabilization of the 1-carboxypropyl radical is the most important factor influencing the course of the reaction. However, hydroxyl radicals prepared by Fenton's method attack positions remote from the carboxyl group in acids (Coffman, Jenner, and Lipscomb 1958) and esters (Beckwith, unpublished data). Evidently hydroxyl radicals have strong electron-acceptor properties and are subjected to polar directive effects by the electron-attracting carbonyl group. Primary alkoxy radicals would be expected to be less electrophilic than hydroxy radicals but more electrophilic than *tert*.-butoxy radicals. In an attempt to verify this prediction the decomposition of *n*-octyl nitrite in *n*-butyric acid has now been studied.

The pyrolysis of alkyl nitrites in the vapour phase has been extensively investigated (Gray and Williams 1959) and is believed to proceed by the following mechanism (Rice and Rodowskas 1935):



A possible alternative to (2) and (3) is the disproportionation of alkoxy radicals (Levy 1953):

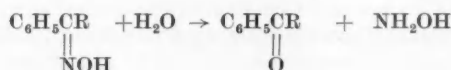
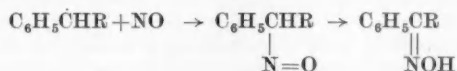
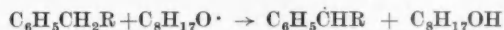


The decomposition of alkyl nitrites in liquid phase probably follows the same sequence of reactions for Kornblum and Oliveto (1949) found that (+)-2-octyl nitrite when heated at 100 °C yielded nitric oxide, octan-2-one, and (+)-2-octanol. An attempt to confirm the formation of *n*-octyloxy radicals from *n*-octyl nitrite by their coupling with 2-cyanopropyl radicals was unsuccessful (Gingras and Waters 1954) but the production of aldehydes and ketones

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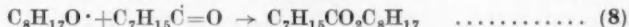
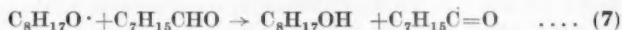
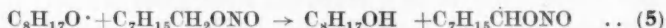
from the hydrocarbon solvents (toluene, ethylbenzene, and diphenylmethane) was attributed to the following reactions:



By analogy with these reactions it was anticipated that the thermal decomposition of *n*-octyl nitrite in *n*-butyric acid would give rise to succinic acid semialdehyde, acetone (from acetoacetic acid), and propionic acid (from α -keto-butyric acid). By the analysis of the reaction mixture for these products it was expected that an estimate of the rates of attack of *n*-octyloxy radicals on the α -, β -, and γ -positions of butyric acid could be made. This aim has not been achieved but the results obtained provide further information as to the mode of decomposition of alkyl nitrites.

When *n*-octyl nitrite was heated at 116 °C in butyric acid the major products were nitric oxide, water, *n*-octanoic acid (23 per cent.), *n*-octyl octanoate (25 per cent.), and *n*-octyl butyrate (51 per cent.). Of these *n*-octyl butyrate and water were undoubtedly formed by esterification of *n*-octanol with butyric acid and there appears to be no evidence of direct free-radical attack on the solvent except perhaps for minute quantities of acetic and propionic acids which were detected by paper chromatography. In agreement with the previous work of Gingras and Waters (1954) no octaldehyde was isolated; this seems to be an important point of difference between the decomposition in vapour and liquid phases.

The mechanism for the formation of the abovementioned products cannot be set down with certainty. The very ready hydrolysis of *n*-alkyl nitrites is well known and it is thus possible that the octyl butyrate was formed by transesterification of octyl nitrite with the solvent. The nitrous acid simultaneously formed might lead to the other products by oxidation reactions. However, the relative yields of octyl butyrate and octyl octanoate indicate that the latter must have been formed directly rather than by subsequent esterification of octanol and it is therefore suggested that it arises by the following route:



These reactions are followed by esterification and cross-esterification respectively of octanol and octyl octanoate with the solvent. Since the hydrogen-abstraction

steps (5) and (7) are competitive the absence of octaldehyde from the reaction mixture indicates that reaction (7) is very rapid. This is in accordance with the high reactivity of aldehydes towards hydrogen abstraction by other types of alkoxy radicals (Rust, Seubold, and Vaughan 1948).

The absence of free-radical attack on the solvent may be attributed to the fact that butyric acid is a poor hydrogen donor compared with octyl nitrite. It thus appears that reactions of alkoxy radicals derived from alkyl nitrites will only be observed in the presence of substrates which are sufficiently active as hydrogen donors to compete successfully with reaction (5). The alkyl-aromatic solvents used by Gingras and Waters (1954) were apparently in this class. Further experiments designed to test these hypotheses are in hand and will be reported at a later date.

Experimental

n-Octyl nitrite (22.6 g, freshly purified by fractional distillation under reduced pressure) and *n*-butyric acid (45.1 g, redistilled) were heated in a vapour-bath (116 °C) under nitrogen. Nitric oxide was evolved and the solution became brown (c. 1 hr) and then slowly faded to a pale yellow colour. After 30 hr the reaction mixture was fractionally distilled through a short Widmer column under reduced pressure. The following fractions were collected: (i) 2.5 g, b.p. 52 °C/100 mm; (ii) 6.7 g, b.p. 100–107 °C/100 mm; (iii) 28.6 g, b.p. 68–72 °C/25 mm; (iv) 0.9 g, b.p. 80 °C/3.5 mm; (v) 2.3 g, b.p. 82–86 °C/3.5 mm; (vi) 15.2 g, b.p. 94–98 °C/3.5 mm; (vii) residue, 6.5 g.

All of these fractions were analysed in the same way. A typical procedure is as follows: the distillation residue (6.5 g) was dissolved in ether and extracted with 10% aqueous potassium bicarbonate. Evaporation of the solvent from the ether layer yielded a neutral oil (4.53 g) while an acid fraction (1.86 g) was obtained by acidification and ether extraction of the aqueous layer. The acid was identified as *n*-octanoic by chromatography on paper with the solvent butanol-1.5*N* ammonia (1:1) when one spot with R_F 0.73, was detected. The *p*-toluidide, m.p. 69 °C, was identical with that derived from authentic *n*-octanoic acid. A sample (1.63 g) of the neutral material was hydrolysed by heating under reflux for 3 hr with a solution of sodium (1 g) in ethanol (25 ml) and water (1 ml). The hydrolysis mixture was poured into water and the neutral product was extracted with ether. It was identified as *n*-octanol (0.81 g) by preparation of the 3,5-dinitrobenzoate, m.p. 63 °C, which was identical with the authentic compound. Acidification of the hydrolysis mixture with dilute sulphuric acid followed by extraction with ether yielded an acid (0.83 g) which was identified as *n*-octanoic by paper chromatography and preparation of the *p*-toluidide.

n-Butyric acid, which was isolated from other distillation fractions, was identified by its R_F value (0.29) on paper chromatography and by preparation of the *p*-toluidide, m.p. 75 °C. Traces of other acids, probably acetic and propionic, were detected by paper chromatography.

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